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SYNTHESIS AND ELECTROCHEMICAL PROPERTIES OF NEW 1,3-DITHIOL-2-YLIDENE DERIVATIVES.

SAMIA AMRIOU

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1 6 JAN 2004

Ph.D. THESIS

2003

**SYNTHESIS AND ELECTROCHEMICAL
PROPERTIES OF NEW 1,3-DITHIOL-2-YLIDENE
DERIVATIVES.**

Samia AMRIOU

**Department of Chemistry
University of Durham**

**A Thesis submitted for the degree of Doctor of Philosophy
at the University of Durham**

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Declaration

The work described in this thesis was carried out in the Department of Chemistry at the University of Durham between October 2000 and September 2002, and January 2003 and September 2003, and at the Institut de Ciència de Materials de Barcelona between October 2002 and December 2002. The author carried out all the work unless otherwise stated, and has not previously been submitted for a degree at this or any other university.

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SYNTHESIS AND ELECTROCHEMICAL PROPERTIES OF NEW 1,3-DITHIOL-2-YLIDENE DERIVATIVES.

Samia AMRIOU

University of Durham (October 2003)

The π -electron donor system 9-(1,3-dithiol-2-ylidene)thioxanthene has been synthesised via Horner-Wadsworth-Emmons reactions of 1,3-dithiol-2-phosphonate ester reagents with thioxanthen-9-one. The electrochemistry of a range of derivatives shows a single, two-electron oxidation wave, which is quasi-reversible. X-Ray crystal analysis reveals a folded structure. Compound **33c** has proved to be a key building block which via lithiation chemistry has provided the hydroxymethyl derivative **37** and hence the synthesis of derivatives with covalently attached fluorenone, dicyanomethylenefluorene and PTM (4-[bis(2,3,4,5,6-pentachlorophenyl)methyl]-2,3,5,6-tetrachlorobenzoyl chloride radical) as electron acceptor substituents has been achieved. Electrochemical, spectroscopic and spectroelectrochemical studies have revealed the presence of intramolecular interactions in these compounds. 9-(4-Iodo-5-methyl-1,3-dithiol-2-ylidene)thioxanthene has been synthesised and shown to undergo clean metal-catalysed cross-coupling reactions under Suzuki and Sonogashira conditions, which is unusual for 1,3-dithiol-2-ylidene derivatives. Aldehyde functionality has been attached to the 9-(1,3-dithiol-2-ylidene)thioxanthene core and reacting these aldehyde reagents with C_{60} and sarcosine gave covalent 9-(1,3-dithiol-2-ylidene)thioxanthene- C_{60} 1:1 diad molecules, and the analogous 2:1 adducts. A second series of compounds, with more extension of the π -system, eg compound **66a**, has been synthesised and characterised by X-ray crystallography, a range of spectroscopic studies and by epr and electrochemistry.

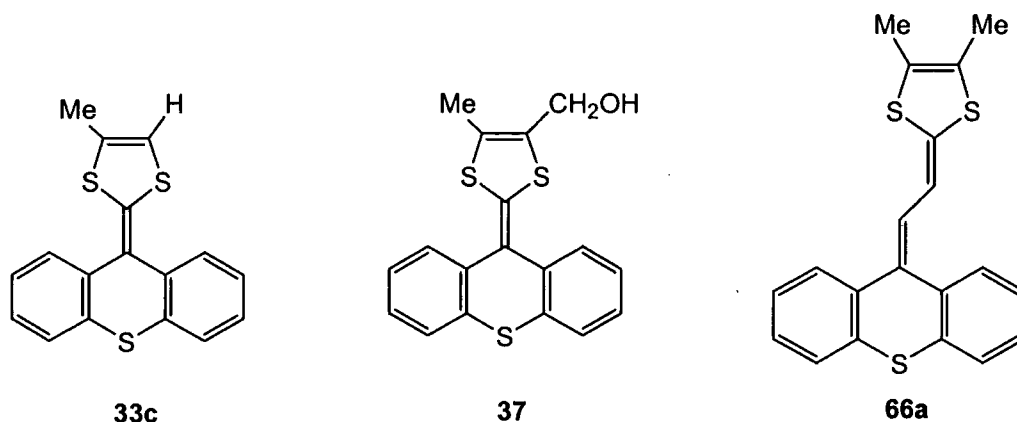


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ABBREVIATIONS

BEDT-TTF	- Bis(ethylenedithio)tetrathiafulvalene
BuLi	- n-Butyllithium
CI	- Chemical ionisation
CT	- Charge-transfer
CV	- Cyclic voltammetry
DCM	- Dichloromethane
DMF	- <i>N,N</i> -Dimethylformamide
DMSO	- Dimethylsulfoxide
EI	- Electron impact
EPR	- Electron paramagnetic resonance
eq.	- Equivalent(s)
ES	- Electrospray
Fc	- Ferrocene
ICT	- Intramolecular charge-transfer
IR	- Infrared
LB	- Langmuir-Blodgett
LDA	- Lithium diisopropylamide
MALDI	- Matrix assisted laser desorption/ionisation
mnt	- [S ₂ C ₂ (CN) ₂] ₂
mp	- Melting point
MS	- Mass spectrometry
NLO	- Non-linear optical
NMR	- Nuclear magnetic resonance
Pc	- Phthalocyanine
PTM	- 4-[bis(2,3,4,5,6-pentachlorophenyl)methyl]-2,3,5,6-tetrachlorobenzoyl chloride radical
rt	- Room temperature
SEEPRE	- Simultaneous electrochemistry electron paramagnetic resonance
T	- Temperature
TCNQ	- 7,7,8,8-Tetracyano- <i>p</i> -quinodimethane
THF	- Tetrahydrofuran
TLC	- Thin layer chromatography
Ts	- <i>p</i> -Toluenesulfonyl (tosyl)
TTF	- Tetrathiafulvalene
TTFAQ	- 9,10-Bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene
UV	- Ultraviolet
vis	- Visible

CHAPTER ONE



I INTRODUCTION

1. Tetrathiafulvalene

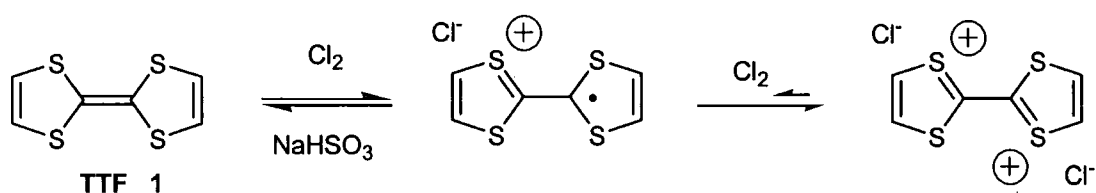
a) Description

The first reliable synthesis of the unsubstituted π -electron donor molecule tetrathiafulvalene (TTF, **1**) can be ascribed to Kiesslich, working in Hünig's laboratory at the University of Würzburg ^[1-3]. TTF **1** was first described in the open literature in 1970 by Wudl *et al* ^[4]. It is interesting to note that dibenzo-TTF had been known since 1926 ^[5] and a mixture of dimethyl-TTFs was reported in 1965 ^[6, 7] but no redox chemistry of the TTF system was described prior to the thesis of Kiesslich ^[1]. The X-ray crystal structure of TTF **1** ^[4] shows an almost planar molecule consisting of two 1,3-dithiole rings linked by a double bond, creating a highly conjugated π -system, each ring containing 7 π -electrons.

The oxidation of TTF, chemically or electrochemically (Figure 1), occurs in two sequential and reversible one-electron waves (Figure 1), forming the cation radical and then the dication, stabilised by the gain of 6 π -electron aromaticity of the 1,3-dithiolium cation. In the dication, although both rings are 6 π -electron systems, the stability of the system is reduced by intramolecular Coulombic repulsion.

Redox activity

-chemical oxidation



-electrochemical oxidation

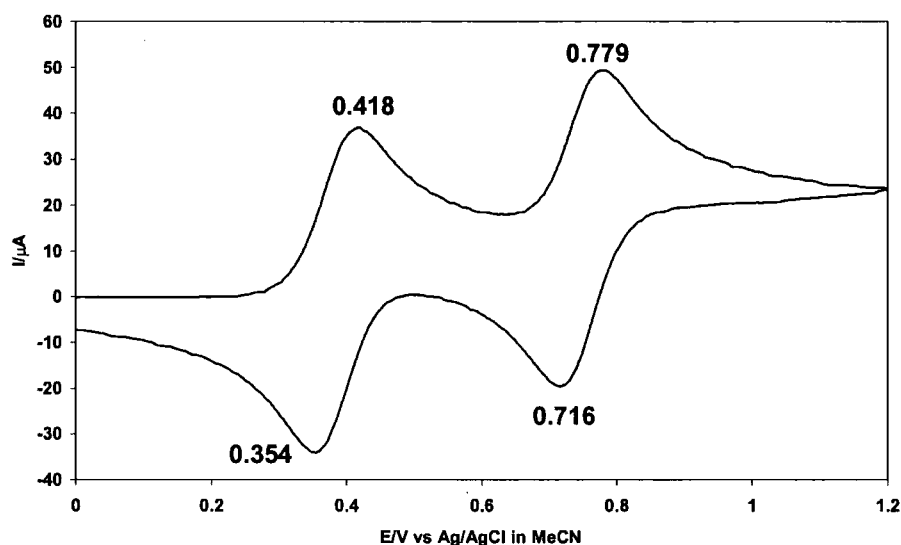
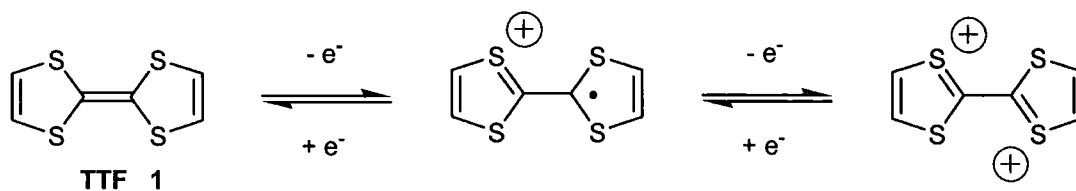
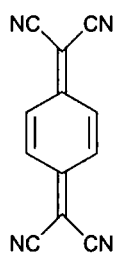


Figure 1. Redox behaviour of TTF.

TTF is an excellent π -electron donor (low oxidation potential), and stacks easily in the solid state when combined with π -electron acceptors to form charge transfer complexes (CTCs). Many of these CTCs possess interesting conductivity and magnetic properties. The CTC of 1:1 stoichiometry formed by TTF and the strong acceptor 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ **2**) is the most famous and relevant CTC, being the first organic metal, which was discovered in 1973^[8,9]. Indeed, the conductivity profile of this CTC showed typical metallic behaviour for $T > 54\text{K}$, (due to the independence of molecular stacks between TTF and TCNQ molecules in the complex, resulting in strongly anisotropic transport properties), with a Peierls transition (metal-insulator) at lower temperature.

The crystal structure of TTF-TCNQ (Figure 2) shows separate stacks of TTF and TCNQ units, with partial charge transfer from TTF to TCNQ. Prior to this work, many semiconducting complexes and salts of TCNQ were known, but none had shown true metallic behaviour^[10].



TCNQ, 2.

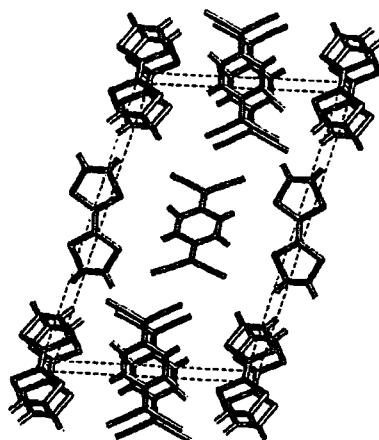


Figure 2. Unit cell of TTF-TCNQ CTC.

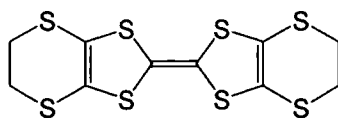
b) Properties

The TTF molecule has generated considerable interest since the beginning of the 1970's, when researchers observed its high electrical conductivity in a chloride salt^[11], and its metallic behavior in the CTC, TTF-TCNQ^[8, 9]. Recently, new applications of TTF and its derivatives in supramolecular and materials chemistry have been developed^[12], making TTF a more versatile building block than was hitherto appreciated. The most important properties of the TTF system are these:

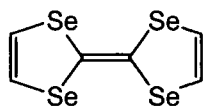
- 1) The oxidation of TTF occurs in two sequential and reversible steps within a very accessible potential window (0.4 to 0.8 V vs Ag/AgCl in a range of organic solvents) and the oxidation potentials can be modified by the attachment of electron donating or electron withdrawing groups.

- 2) The cation radical is thermodynamically very stable due to a gain of aromaticity, and UV/vis absorption spectra of the three TTF redox states show clearly distinguishable features.
- 3) TTF derivatives, especially the cation radicals, easily form dimers, highly ordered stacks, or two-dimensional sheets.
- 4) The TTF ring system is stable to many synthetic transformations, although oxidising agents and strongly acidic conditions should be avoided.
- 5) The TTF molecule is conformationally very flexible, because folding can occur about the S...S axes of the dithiole rings, although strongly-folded derivatives (notably cyclophane derivatives ^[13, 14] lose the reversible redox activity of the more planar derivatives.

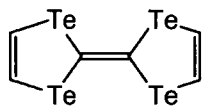
A lot of time has been invested in the design of new π -donors by modification of the TTF framework in order to increase the thermodynamic stability of the cation radical and/or to control the intermolecular architecture in derived salts and CTCs. The importance of the two-dimensional interaction through intermolecular non-bonding S...S contacts in the charge transfer salts has been recognised in order to suppress the metal-insulator transition which is characteristic of most one-dimensional organic metals at low temperature ^[15]. It has usually been achieved by introduction of alkylchalcogeno substituents onto the TTF skeleton, notably bis(ethylenedithio)TTF (BEDT-TTF) and/or the exchange of the sulphur atoms of TTF with the larger chalcogenides selenium (TSF) and tellurium (TTeF) ^[16].



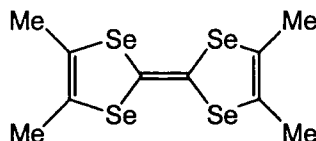
(BEDT-TTF)



(TSF)



(TTeF)



(TMTSF)

Indeed, the study of tetramethyl-TSF (TMTSF) led to the first organic superconductors ($T_c = 1\text{--}2\text{ K}$) of formula $(\text{TMTSF})_2\text{X}$ ($\text{X} = \text{PF}_6^-$, AsF_6^- , TaF_6^- , NbF_6^- , ReO_4^- and ClO_4^-) which were reported by Bechgaard *et al* in 1980 and 1981 [17, 18]. Within this series only the perchlorate salt is a superconductor at ambient pressure: the others require the application of high pressure (5-12 kbar) to the crystals before superconduction is observed. X-Ray analysis reveals that the tetrahedral ClO_4^- anions are located within channels in the stacked structure in an asymmetric environment with numerous short $\text{H}\cdots\text{O}$ contacts (i.e. donor...anion stabilising interactions) [19].

In the last 20 years several other families of tetrachalcogenofulvalene-based superconductors have been synthesised. The most important are the salts of BEDT-TTF of formula $(\text{BEDT-TTF})_2\text{X}$ for which in 1990 T_c was raised to 11.6 K in $\kappa\text{-(BEDT-TTF)}_2[\text{Cu}(\text{CN})_2]\text{Br}$ [20] and 12.8 K in $\kappa\text{-(BEDT-TTF)}_2[\text{Cu}(\text{CN})_2]\text{Cl}$ under applied pressure of ca. 0.3 kbar [21].

The structures of these salts are based on a kappa-packing motif (orthogonal dimers) of BEDT-TTF molecules and a polymeric network of anions, i.e. they are markedly different from the planar stacks of TTF or TMTSF moieties in the TTF-TCNQ complex or $(\text{TMTSF})_2\text{X}$ salts. It seems that a key feature of the BEDT-TTF molecule in this regard is that the ethylenedithio units are conformationally flexible. To date, many reported modifications to the BEDT-TTF skeleton, e.g. incorporation of O or Se atoms,

or attachment of peripheral substituents, have not further raised T_c values in derived salts [22]. Only the fullerene-based systems [23, 24] have higher T_c values for organic superconductivity.

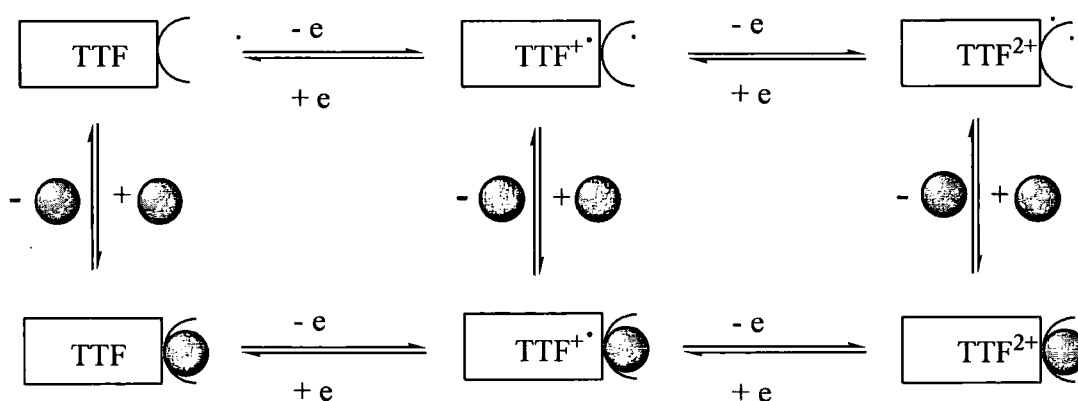
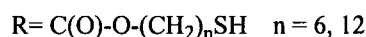
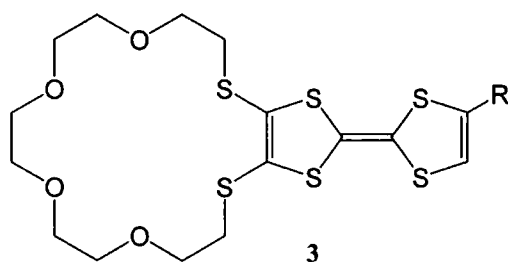
c) Other Applications of TTF and its Derivatives

For many years the difficulties of synthesising many TTF derivatives (especially unsymmetrical ones) in practically useful quantities hindered the development of TTF in the wider context of materials chemistry. However, recent advances in synthetic TTF chemistry have changed this situation: (i) TTF itself is now available in 20 g batches from cheap starting materials [25] (ii) a lithiation/electrophilic substitution approach provides a wide range of substituted derivatives of TTF in high yields [26-28] (iii) selective protection/deprotection reactions of thiolate groups attached to 1,3-dithiole-2-thione-4,5-dithiolate (dmit) precursors and TTF systems, readily yield multi-gram quantities of new TTF building blocks [29, 30].

TTF derivatives now play an important role as redox sites in diverse areas of supramolecular chemistry. One of the first applications concerns their use as cation sensors [31, 32] (Scheme 1). Researchers have observed that TTF derivatives with macrocyclic substituents are efficient as cation sensors because binding of a metal analyte to the macrocyclic ligand leads to a change in the optical and redox properties of the TTF part. Such crown-annelated TTFs were first synthesised by Otsubo and Ogura [33] and their metal-binding characteristics were explored by Becher *et al* [34, 35] and in our laboratory [36]. In particular, the oxidation potential for the $\text{TTF}^0/\text{TTF}^+$ redox couple is shifted in CV experiments to more positive potentials when a metal atom is bound within the adjacent cavity, due to intramolecular Coulombic repulsion. Further electrochemical oxidation leads to expulsion of the guest cation, thus representing an electrochemically-driven reversible host-guest system. The second oxidation potential of the TTF is usually unchanged by metal binding/expulsion and acts as a convenient internal reference. This is a benefit of TTF over other systems (e.g. ferrocene derivatives), which undergo only one reversible redox wave.

The voltammetric effects of metal binding with TTF-crown systems are generally small (< 100 mV shifts), although they are highly reproducible and quantitative. Self-assembled monolayers (SAMs) represent an attractive method for device fabrication, having the advantage of straightforward preparation and good stability. Earlier work in our laboratory established that SAMs of TTF derivative **3** adsorbed on platinum give the typical two-wave response of the TTF system and the electrochemical recognition of metal cations by SAMs of **3** was clearly demonstrated with positive potential shifts upon metal binding, similar to those observed in solution, *e.g.* $\Delta E_{1/2}$ for Li^+ and K^+ = 10-20 mV; for Na^+ and Ba^{2+} = 45-55 mV and for Ag^+ = 75-80 mV ^[37, 38]. This is an important advance in the development of nanoscale sensors and molecular devices.

New TTF SAMs and their cation recognition properties have also been reported by other workers ^[39].

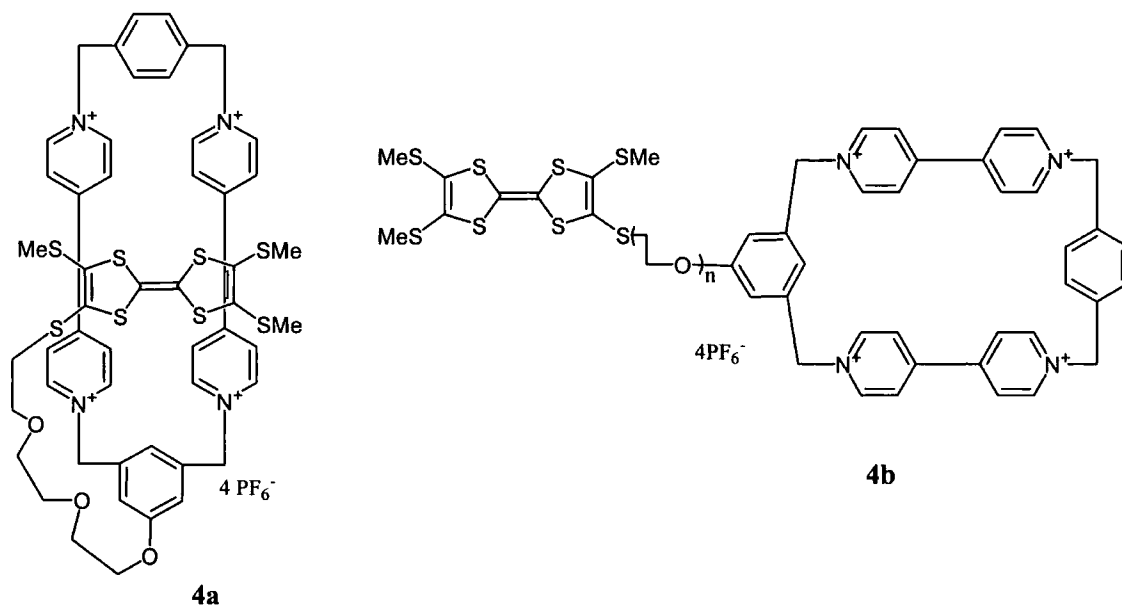


Scheme 1: Mechanism for metal ion recognition

TTFs have also been exploited as liquid crystalline derivatives due to their ability to form stacked structures and to transport charges. Research groups have observed that the supramolecular architecture of spin-coated films, under certain conditions, can be changed simply by oxidation or by heating ^[40].

Intramolecular charge transfer processes between TTFs donors and acceptors are very relevant in the study of dyes, nonlinear optics, and light-harvesting systems ^[12, 22]. A wide range of acceptors, such as fullerenes, quinones or phthalocyanines, have been covalently attached to TTFs donors to form complexes and then study their ICT properties. For instance, photoinduced ICT have been reported for phthalocyanine-TTF complexes, and for some of them it has been observed that the fluorescence of the phthalocyanine can be quenched to changing degrees by varying the spacer unit between the Pc and TTF moieties.

The field of molecular switches is currently very important. Becher and coworkers have developed the 'self-complexing' intramolecular CT (ICT) interaction of a designed TTF molecule with an attached cyclobis(paraquat-*p*-phenylene) π -acceptor to obtain a thermally-controlled switch ^[41]. Refluxing the green-coloured equilibrium solution (λ_{max} 785 nm) of **4a** (complexed) and **4b** (decomplexed) caused almost complete disappearance of this ICT band, demonstrating conversion to the orange-coloured decomplexed form **4b**. Storing the solution at room temperature for *ca.* 20 h re-established the green colour. This cycle could be repeated with only a small decrease in the equilibrium absorbance after each experiment.



A more elaborate system which can be switched reversibly between three distinct states by electrochemically changing the redox state of the TTF unit in the presence of two hosts with differing π -donor/ π -acceptor capabilities, *viz.* cyclobis(paraquat-*p*-phenylene) and 1,5-dinaphtho[38]crown-10 has been developed ^[42]. It was established that neutral TTF (as an electron-donor guest) is complexed by the electron-acceptor paraquat cyclophane, the TTF cation radical is not bound by either of the hosts, and the π -electron accepting TTF dication is bound within the macrocyclic polyether cavity. Electrochemical experiments revealed that the three-component mixture behaves as a reversible three-pole switch. Potential applications in electrochromic displays were noted as the three states have different colours and can be interconverted by changing the potential in an easily accessible range (from +0.3 to +0.8 V *vs* SCE). Very recently, comparable studies using a self-assembled (surface-confined) TTF analogue on gold substrates have been performed ^[43].

Finally, TTF has been developed in polymer chemistry through the incorporation of TTF units in main chains and side chains of polymers in attempts to improve the conductivity along the polymer chains ^[44-46]. Researchers have succeeded in forming different types of films with these TTF polymers, e.g. by spin coating or electropolymerisation of monomer units ^[47]. In general, studies of their properties have

been limited by lack of solubility or processability of the polymers. Compared to analogous linear polymers, TTF-containing dendrimers generally possess good solubility in a range of organic solvents, which has enabled their properties to be well characterized. Notably these macromolecules display very clean multi-electron redox behaviour and provide some of the first all-organic dendritic poly(radical cations) and poly(dications), which can be considered as highly-charged organic nanoparticles^[48-51].

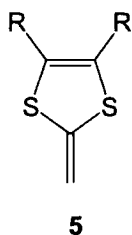
2. 1,3-dithiol-2-ylidene ring

a) General Properties

The synthesis of redox-active building blocks with reactive functional groups is of great importance in supramolecular and materials chemistry. As outlined above, TTF has been widely explored, and a vast number of its derivatives reported. They remain of major interest due to the remarkable redox properties of the TTF framework. However, there is a continued need to explore new π -electron donor systems, with different redox, optoelectronic and structural properties, which can be readily functionalised. Thus, other 1,3-dithiol-2-ylidene derivatives (apart from TTF) have proved to be very interesting compounds for different reasons^[52, 53].

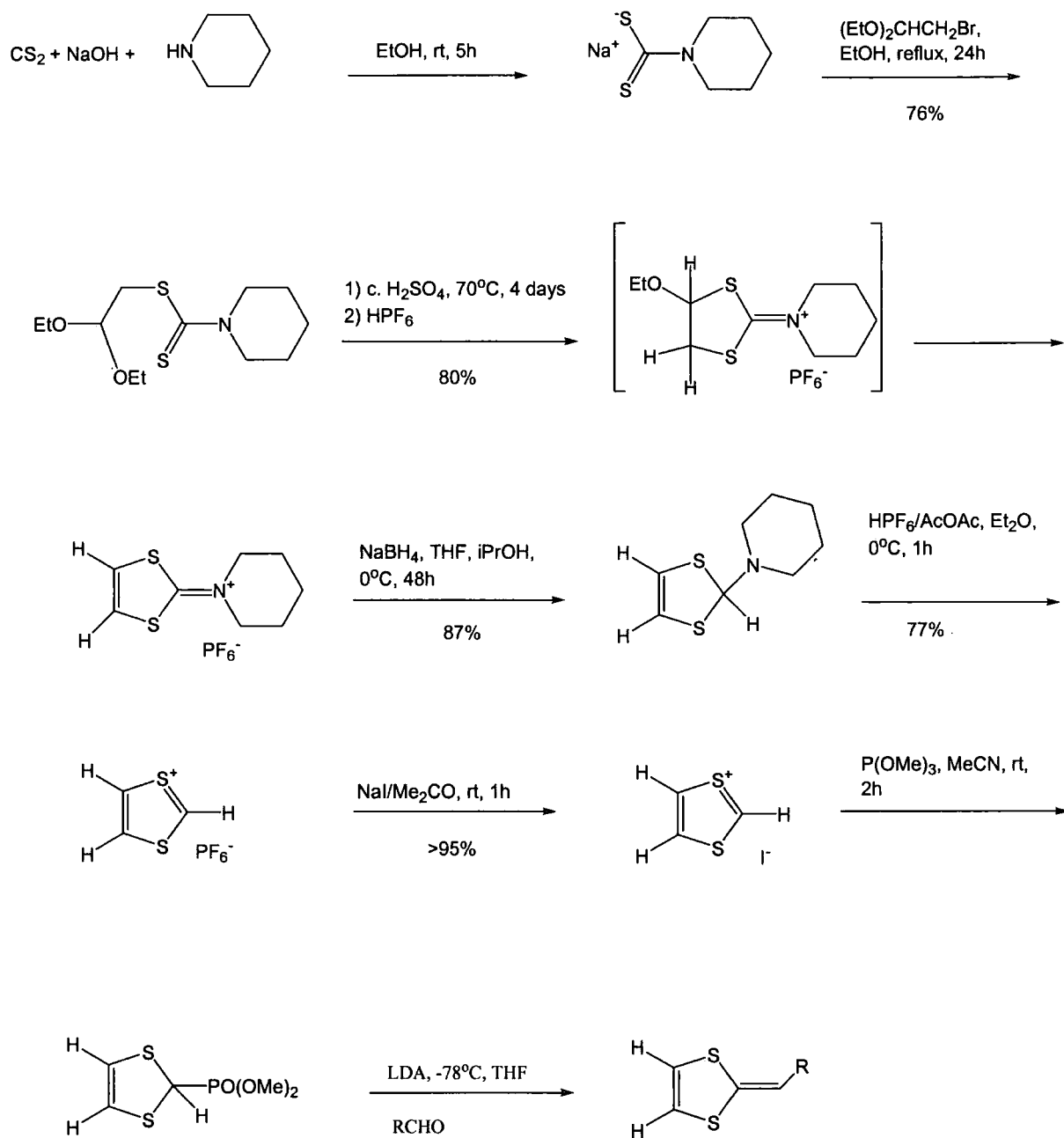
Firstly, the properties of the 1,3-dithiol-2-ylidene ring system **5** can be easily modified by attachment of a range of functional groups present in the C-4 and C-5 positions. Secondly, the system **5** is readily oxidised to the stable six π -electron 1,3-dithiolium cation radical species, although oxidation potentials are generally higher than for TTF. The nature of the substituents attached to the exocyclic methylene carbon will clearly be important in determining the stability of the oxidised species. Also, the presence of polarisable sulphur atoms and the planarity of the 1,3-dithiolium cation assist in close intermolecular interactions in the solid state due to π - π overlap. A combination of these properties has resulted in the 1,3-dithiol-2-ylidene unit being a key structural feature in many new π -electron donors, conducting polymers, Langmuir-Blodgett film

materials, sensors, molecular shuttles, as well as potential nonlinear optical, and ferromagnetic materials.



b) Synthesis of the 1,3-dithiol-2-ylidene ring

Many literature routes have been reported for the synthesis of derivatives of this unit, and Moore and Bryce^[25] have developed a cheap, reliable, large-scale (ca. 25-50 g) route to the key building blocks for this system. Through several stages, this route leads to the formation of the corresponding phosphonate ester used then for Horner-Wadsworth-Emmons olefination reactions with aldehyde or ketone partners (Scheme 2).

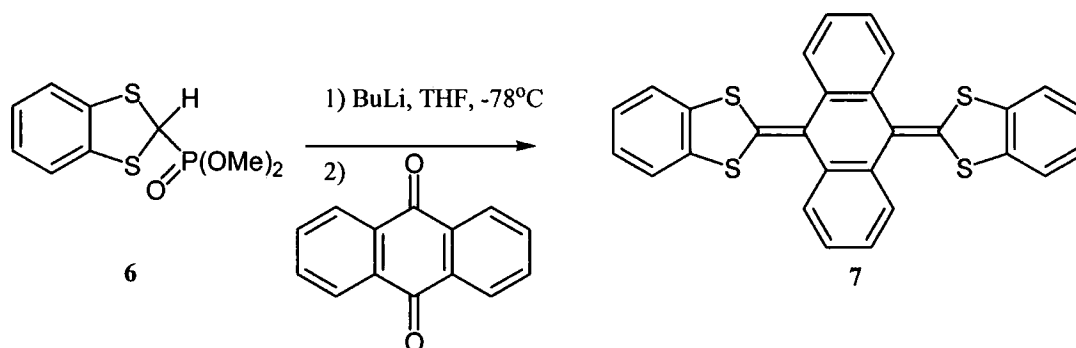


Scheme 2. Synthesis of the 1,3-dithiol-2-ylidene ring ^[25].

3. Anthracene-TTF

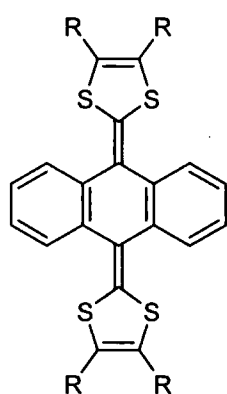
a) Synthesis of Anthracene-TTF derivatives

Double Horner-Wadsworth-Emmons reactions of 1,3-dithiol-2-phosphonate ester reagents with anthraquinone and its derivatives have produced a particularly interesting series of π -electron donors. The first such derivative, namely 9,10-bis-(1,3-benzodithiol-2-ylidene)-9,10-dihydroanthracene **7** was synthesised by Akiba *et al.* ^[54] using the phosphonate ester **6** reagent and anthraquinone in 78% yield (Scheme 3). However, the properties of compound **7** were not explored in any detail.

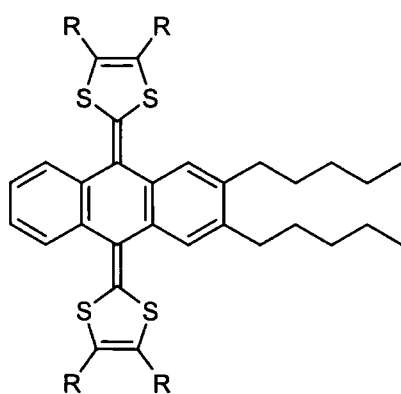


Scheme 3. Synthesis of dibenzo-anthracene-TTF **7**.

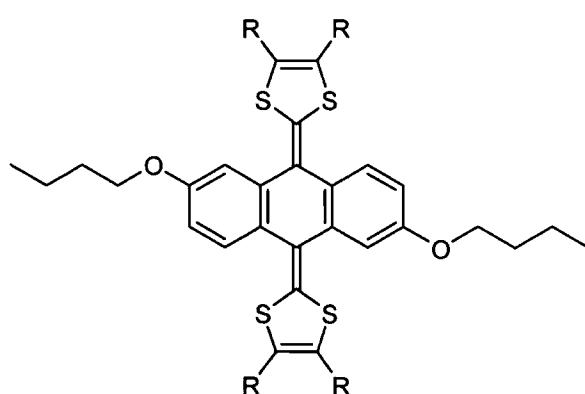
Following this general scheme, using appropriate phosphonate ester reagents, symmetrical anthracenediylidene derivatives have been synthesised in order to study their charge transfer complexes (**8a-c**) ^[55], and to study the electrochemistry in detail by increasing the solubility of the system (**9, 10**) ^[56, 57].



8 a R= H
b R= Me
c R= SMe

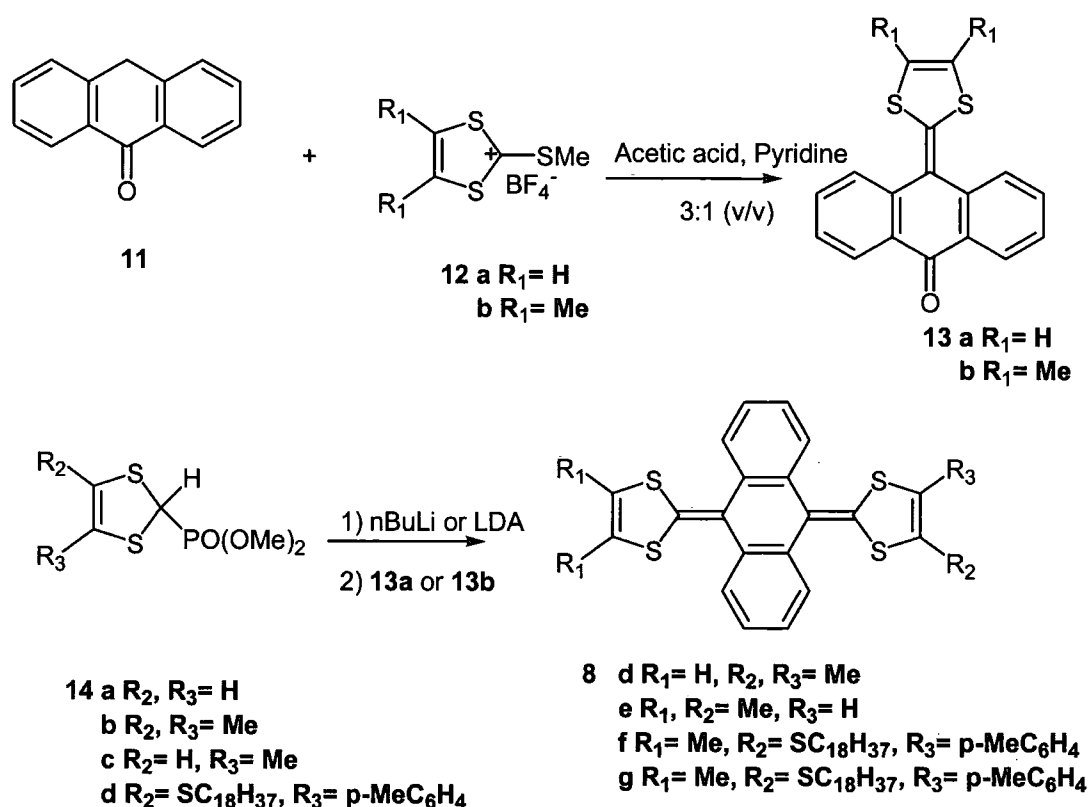


9



10

Unsymmetrical derivatives have been synthesised following a two-step methodology ^[58]. First, the reaction of the anion of anthrone **11** with 1,3-dithiolium cations **12a,b** afforded anthrone derivatives **13a,b**. A Horner-Wadsworth-Emmons reaction using phosphonate esters **14a-d** on **13a,b** then allowed the formation of unsymmetrical anthracenediylidenes **8d-g** (Scheme 4).

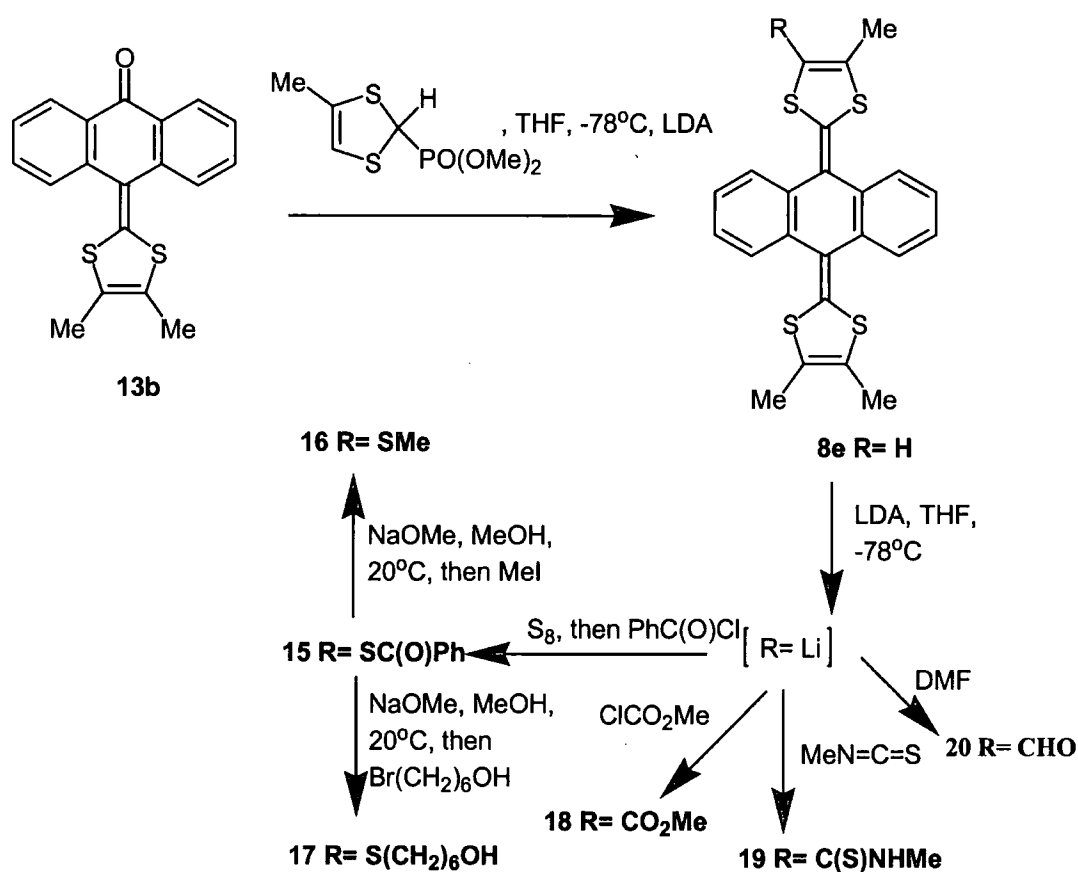


Scheme 4. Synthesis of unsymmetrical anthracene-TTF derivatives.

b) Functionalisation of anthracene-TTF

The synthesis of a new and versatile range of derivatives of **8a**, which contain a reactive functional group attached to one of the 1,3 dithiole rings has been achieved recently in our group. These derivatives were designed to enable system **8a** to be exploited as a functionalised building block in the field of supramolecular and materials chemistry. Hitherto, the known derivatives of **8a** were restricted to those with simple alkyl, thioalkyl or aryl substituents on the dithiole rings, which are not suitable for further functionalisation. Heterocyclic analogues, and a few derivatives with substituents attached to the anthracenediylidene spacer have also been reported^[59]. The functionalisation shown in Scheme 5 was performed using lithiation and trapping of the resulting lithiated species with selected electrophiles. To avoid a problem of precipitation of the lithiated species at low temperature, and to ensure that monolithiation occurred, the

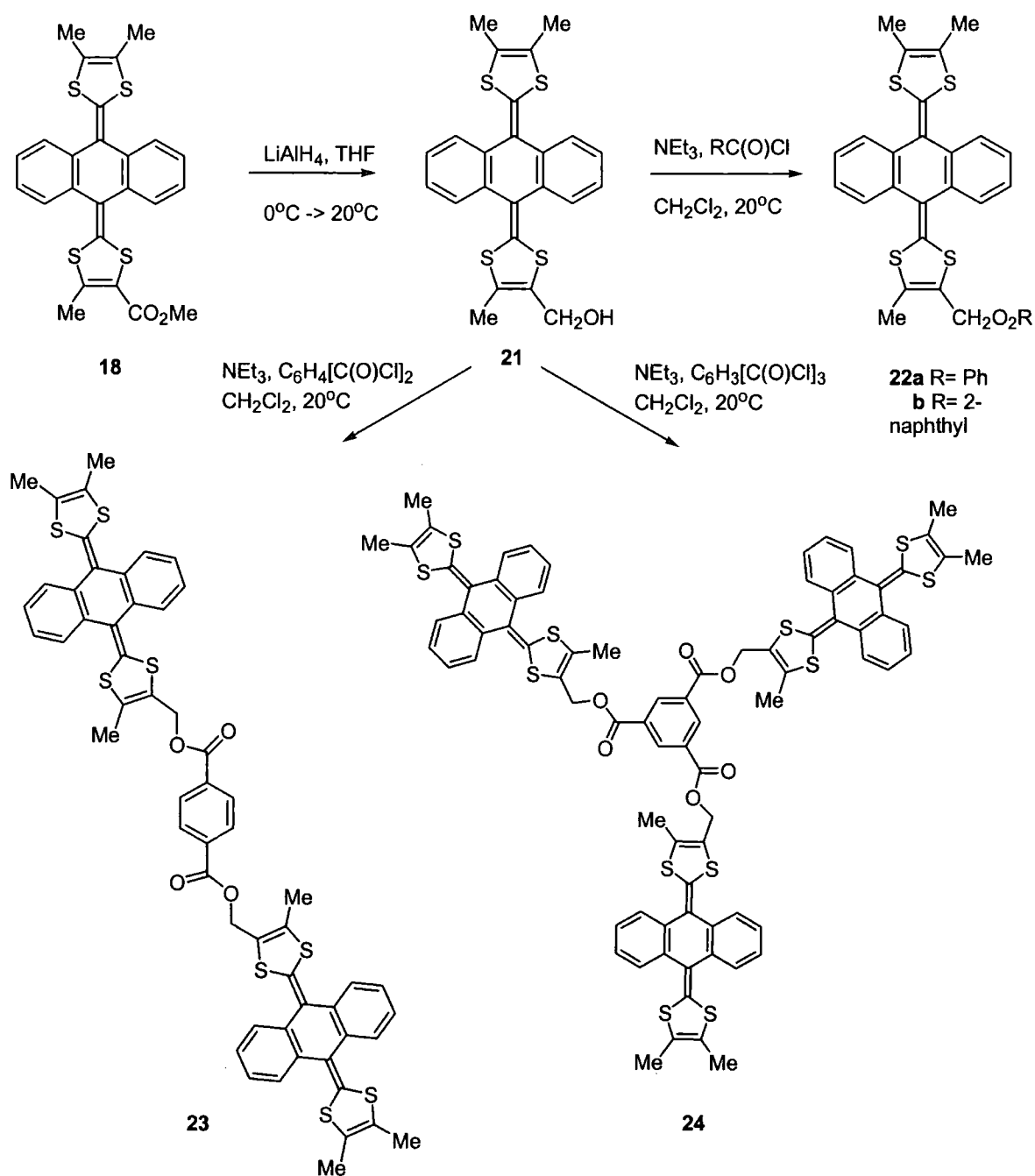
trimethyl derivative **8e** was considered to be the best starting material ^[59, 60]. Using methyl chloroformate as the electrophilic trapping agent proved to be a very efficient way to obtain the methyl ester derivative **18**. Sulfur insertion followed by addition of benzoyl chloride, gave the thioester derivative **15** which is a convenient precursor of other mono-functionalised derivatives **16**, **17**. This Scheme set the precedent for some of the new work described in Chapters 2 and 3 of this thesis.



Scheme 5. Reactions based on species **13b**.

Another route has been developed from compound **18**, which has yielded further functionalised derivatives, some of which have been shown by X-ray crystallographic

studies to engage in intermolecular hydrogen bonding thereby providing increased supramolecular order in solid state structures^[61] (Scheme 6).



Scheme 6. Synthesis of mono-functionalised anthracene-TTF.

c) Redox Behaviour and Structural Features

Some fascinating properties of the anthracene-TTF system have been discovered ^[60].

1. It displays unusually high electron donor ability due to reduced intramolecular Coulombic repulsions in its oxidised states, and gain in anthracene aromaticity as well as dithiolium ring aromaticity. The CV is characterised by a single, two-electron quasi-reversible oxidation wave to yield a thermodynamically stable dication (Figure 3), with electron withdrawing and electron donating substituents on the dithiole rings shifting this wave to more positive and more negative potentials, respectively. The negative shift observed for the reduction of the dication to the neutral form in the CV experiments can be explained by the large change of conformation and loss of aromaticity accompanying this process.

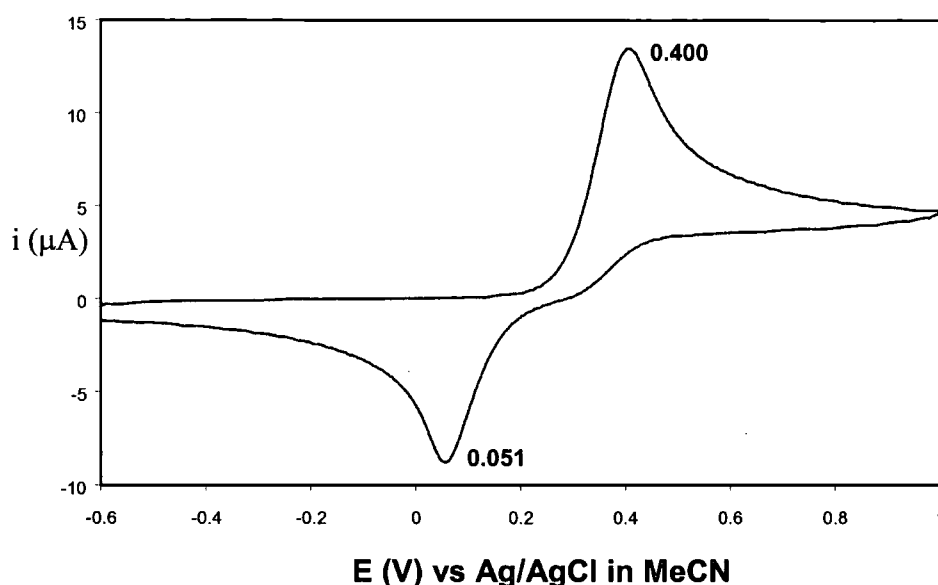


Figure 3. Cyclic voltammetry of trimethyl-anthracene-TTF **8e**.

2. The ring system possesses an unusual saddle-shaped structure (Figure 4(a)), which is enforced by the boat conformation of the central anthracenediylidene ring, which arises as a consequence of steric crowding of the sulphur atoms and the peri hydrogens. X-Ray crystal structures of several derivatives establish that upon oxidation the central

anthracene ring becomes fully aromatic and planar, with the 1,3-dithiolium cations almost orthogonal to this plane (Figure 4(b)). These properties make this system fundamentally different from TTF, which undergoes two, sequential and reversible, single-electron oxidation waves, and is essentially planar as the neutral and radical cation species, although the TTF dication is twisted around the central C-C bond.

These structural features of TTFAQ were first reported in 1990^[62] from crystallographic data, and have been explained since then by theoretical calculations^[63]. ¹H NMR studies have shown that similar conformations of anthracene-TTF exist in solution^[61].

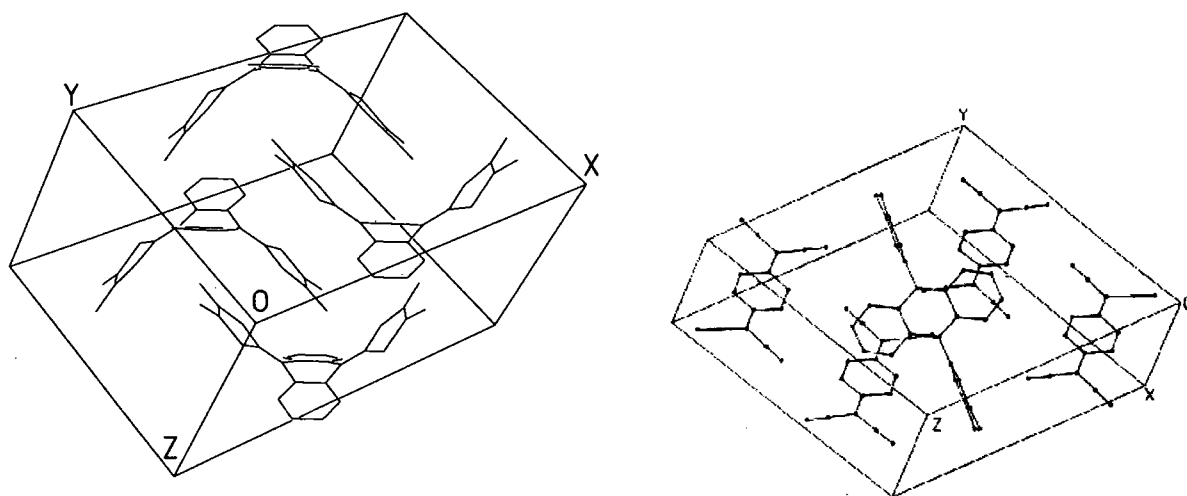


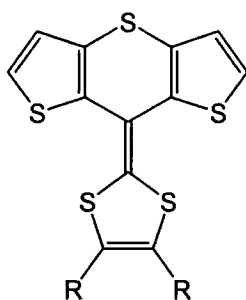
Figure 4

(a) Unit cell of the neutral form of the tetramethyl-anthracene-TTF **8b**^[62].

(b) Unit cell of the dication of the tetramethyl-anthracene-TTF oxidised by TCNQ^[62].

d) Effects of S...S interactions

System **25** is another 1,3-dithiol-2-ylidene derivative, which is of considerable interest, and is relevant to the work described later in this thesis. Intermolecular interaction through short S...S contacts has been known to play a significant role in determining the solid state properties of organic molecular crystals. Noteworthy examples include the superconducting behaviour in the cation radical salts of BEDT-TTF derivatives as well as the electrical conduction of certain sulphur heterocycles as a single component. For instance, cyclic voltammograms of **25a** and **25b** showed two pairs of reversible waves corresponding to the two sequential, one-electron oxidations. The first oxidation potential (E^{ox} vs. SCE in MeCN) of **25a** (+0.32 V) is very close to that of TTF (+0.31 V), and that of **25b** (+0.45 V) is lower than that of dibenzo-TTF (+0.57 V), indicating the strong electron donating properties of **25a** and **25b**. It is noteworthy that the second oxidation potentials of **25a** (+0.45 V) and **25b** (+0.52 V) are much lower than those of TTF (+0.68 V) and dibenzo-TTF (+0.89 V). Quite small differences between the first oxidation potential and the second one correspond to the facile oxidation of $\mathbf{25}^{\cdot+}$ to $\mathbf{25}^{2+}$, showing the reduced Coulombic repulsion on the molecular skeleton of **25** compared with those of TTF derivatives [64].



25 a R= H
b R= CH=CH

These redox properties can be explained by the X-ray crystal structures of the neutral and oxidised state of **25b** (Figure 5).

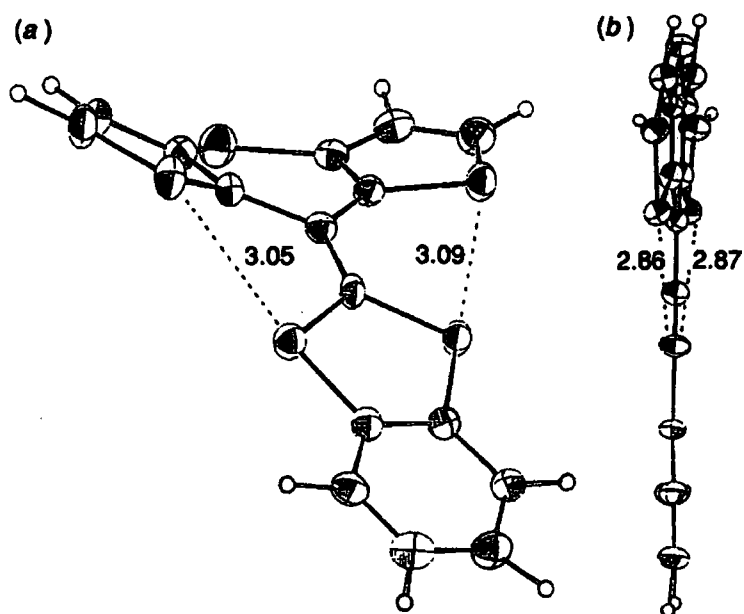
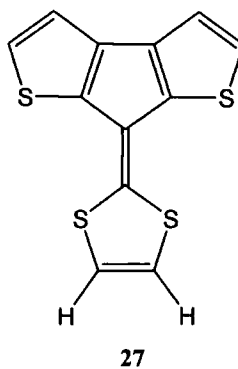
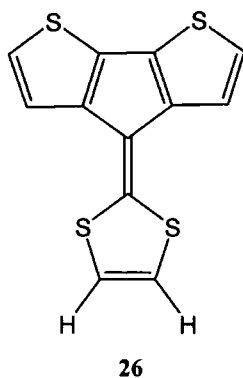


Figure 5. ORTEP drawings of the butterfly-shaped neutral **25b** (a) and the side view of planar **25b⁺** (b). Intramolecular S...S contacts are shown by broken lines ^[64].

Indeed, in the neutral state, the intramolecular distances for S...S are shorter than the sum of van der Waals radii, showing the presence of an attractive interaction between them, resulting in a non-planar geometry of the molecule. By contrast, the cation radical is endowed with molecular planarity. Similar observations have been noted for analogous derivatives **26** and **27** ^[65].



Both compounds show a single irreversible oxidation wave in their cyclic voltammograms. The X-ray structural analysis of **26** shows an almost planar structure, where three intermolecular S...S contacts, which are shorter than the sum of the van der Waals radii, are observed between the thiophene rings of two separated molecules. On the other hand, the X-ray structural analysis of **27** also reveals that the molecule is almost planar, but with two intramolecular S...S contacts which are shorter than the sum of the van der Waals radii. Such short contacts may facilitate the delocalisation of electrons. A short intermolecular S...S contact is also observed between the 1,3-dithiole rings of two separated molecules.

In summary, derivatives of **25**, fused with thiophene units, are found to have strong electron donor strengths comparable with TTF, and although the neutral form of **25** possesses a non-planar geometry, the radical cation is planar. Derivatives of **26** and **27** exhibit low oxidation potentials and X-ray structural analyses show that both molecules adopt planar structures with short intermolecular S...S contacts^[15].

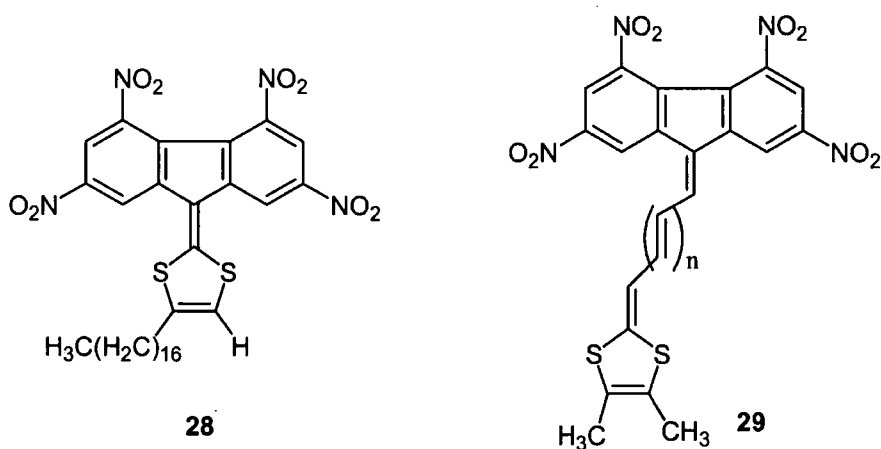
e) Properties

e.1. Donor-acceptor complexes

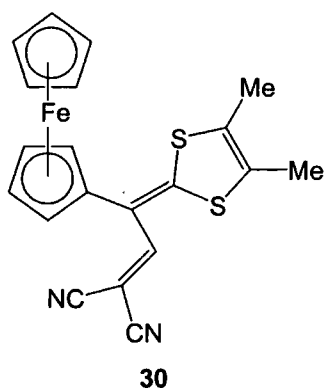
Different π -electron acceptors have been covalently attached to 1,3-dithiol-2-ylidene units generating ICT systems. The chief interest in such molecules is to study the intramolecular electronic interactions, the extent of conjugation between the donor and the acceptor moieties, and the orientation of the stacking between the molecules.

For example, interesting results were obtained on fluorene acceptors with ICT from a 1,3-dithiole donor moiety (**28**, **29**). These complexes are very promising candidates for electron or hole transport materials with high photosensitivity in the long-wavelength and near IR regions of the spectrum. The long alkyl chain in **28** was attached to facilitate solubility. Extending the π -conjugation in **29** (i.e. increasing n) leads to a red shift in the absorption properties, with λ_{max} shifted into the infra red region (690 nm in acetone solution) for $n = 2$ ^[66]. Other promising applications of such push-pull compounds are in

the design of single-component organic semi-conductors, non-linear optical materials, and conductive polymers with a low band gap ^[67].



Much work has also been done on compounds comprising a 1,3-dithiole ring as the π -donor and a dicyanomethylene group as the π -acceptor. Such molecules displayed moderate NLO properties ^[68]. Ferrocene, like 1,3-dithiole, is an electron donor with a half wave potential $E^{1/2} = 0.36$ V (vs Ag/AgCl) comparable to that of TTF (0.34 V), which readily forms charge-transfer complexes. A ferrocenyl group, covalently linked to a dithiole or a TTF system, has been shown to increase the stability of the cation radical produced upon oxidation. Thus the first D- π -A system containing dithiole and ferrocenyl donor units, **30**, has been synthesised in order to explore the effect of this structural modification on intramolecular charge-transfer properties. An X-ray crystal structure was obtained and an ICT band was observed at λ_{max} 491 nm in DCM solution ^[68].

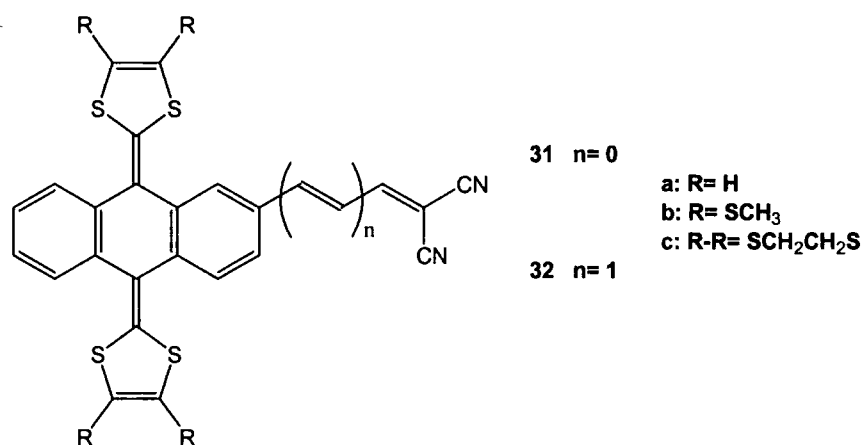


e.2. Cation sensors

Another interest has emerged in the synthesis of crown ether derivatives of anthracene-TTF derivatives ^[69, 70] (Figure 8). By analogy with crown annelated TTFs, discussed above, it was recognised that the system **8** should act as a redox-responsive centre, which would be sensitive to the uptake and release of metal cations at the adjacent intramolecular ionophoric site. Indeed, it was shown that the cation binding induces a shift in the redox potential of the two-electron wave and the complexing ability of the ligand can be switched on or off by varying the applied electrochemical potential. The extended anthracenediylidene chromophore gave a better probe, compared to TTF analogues, for monitoring the metal binding properties of the system by UV-vis spectroscopy.

e.3. Non-Linear Optical properties

In a quest for materials that possess intramolecular charge transfer (ICT) and which may display NLO properties, molecules with π -donor and π -acceptor substituents on opposite end of a conjugated chain (D- π -A) are of great importance ^[68, 71-73]. The anthracene-TTF system has been explored in the design of NLO chromophores. For instance, compounds **31**, **32** have been reported by Martín *et al.* to be efficient NLO chromophores possessing high second order optical non-linearity ($\mu\beta_0$ ca. $150 \cdot 10^{-48}$ esu for **31a-c** and $\mu\beta_0$ ca. $300 \cdot 10^{-48}$ esu for **32a-c**) ^[73].



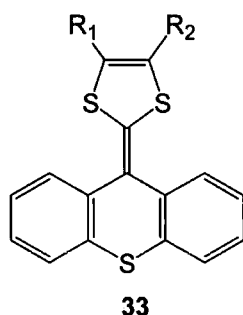
AIMS OF THE PROJECT

Anthracene-TTF derivatives have been developed in our laboratory and found to be very interesting π -electron donors for which an unusual saddle shape confers interesting properties to the system. They can be readily functionalised (i.e. act as good building blocks) and they are oxidised to the dication species, a process occurring with a dramatic change in the conformation of the molecular framework. These studies provided the impetus for the project.

Thus, at the outset of this project we aimed to build on previous work with TTF, anthracene-TTF and related 1,3-dithiol-2-ylidene derivatives by synthesising and characterising derivatives of system **33**. It was of interest to study its electrochemistry and structural properties, and then to attempt to isolate the oxidised species to define its X-ray structure, and to compare it with the structures of related radical cation or dication species, and with the results of theoretical calculations.

We considered also the synthesis and characterisation of derivatives of **33** with electron acceptor units attached to study intramolecular charge transfer. As the project developed we decided to synthesise and characterise extended derivatives of **33**, by increasing the conjugation within the molecule, in order to first lower the oxidation potential of the system, and then to obtain a more planar structure which could facilitate the formation of crystalline salts.

Finally, we targeted the synthesis of push-pull complexes incorporating C_{60} as the acceptor moiety in order to study their electrochemical and UV-vis spectroscopic properties.



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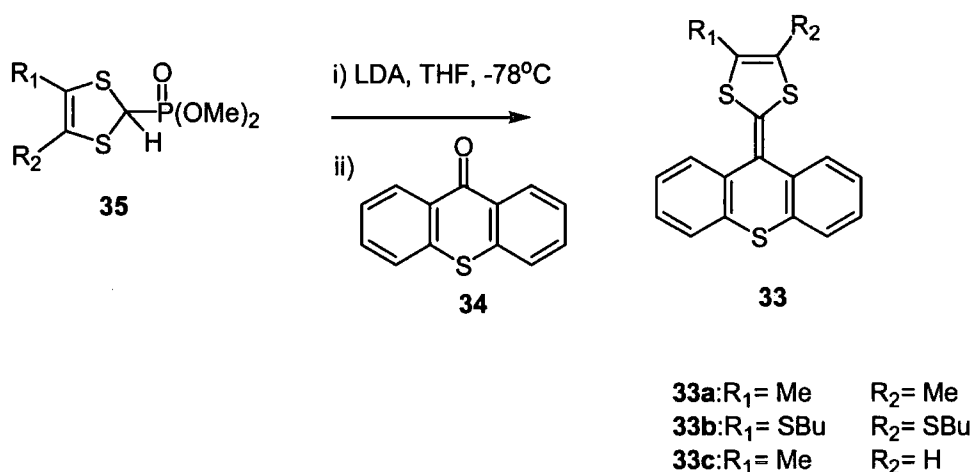
CHAPTER TWO

9-(1,3-DITHIOL-2-YLIDENE)THIOXANTHENE DERIVATIVES

Research in the field of organic conductors such as the TTF family has stimulated a great deal of work on the synthesis of a wide variety of TTF analogues. Different modifications to the basic TTF framework leading to new functionalised π -donors have been studied, in particular those incorporating one, or more, 1,3-dithiol-2-ylidene unit(s). This Chapter describes our investigations into a hitherto unexplored π -electron donor system, namely 9-(1,3-dithiol-2-ylidene)thioxanthene derivatives.

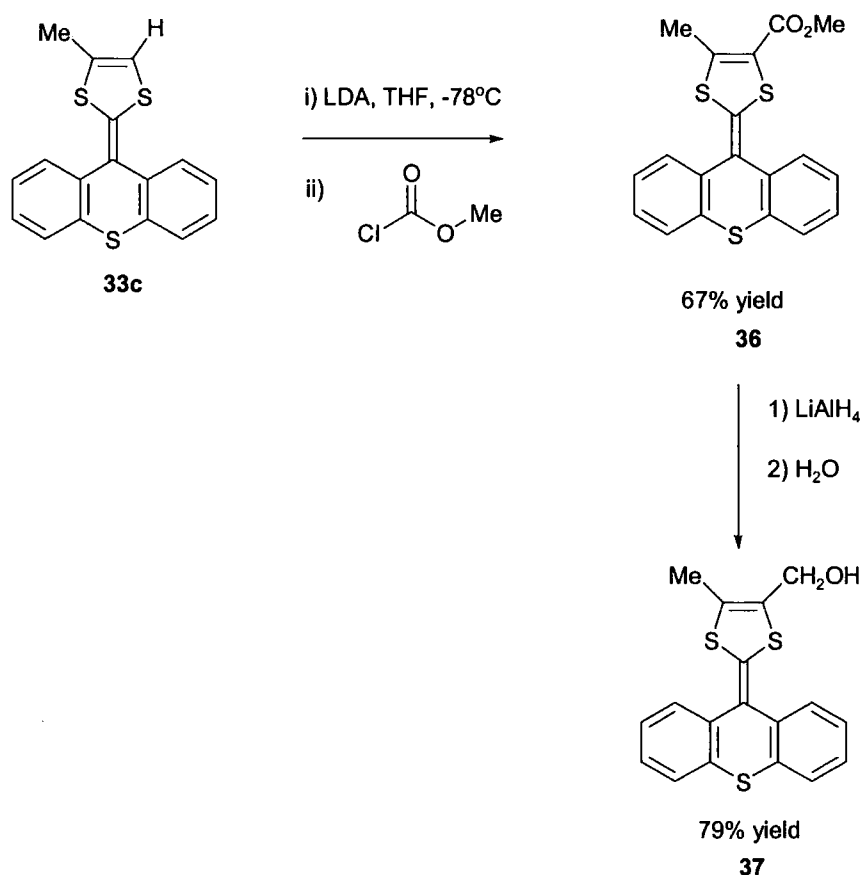
1) Synthesis

The synthesis of 9-(1,3-dithiol-2-ylidene)thioxanthene derivatives was achieved following the literature procedures for reactions of the corresponding phosphonate esters **35a-c** which were synthesised as described ^[1]. They were easily deprotonated with one equivalent of lithium diisopropylamide (LDA) in dry THF at -78°C , then slow addition of thioxanthen-9-one **34** to the reaction mixture gave the expected Horner-Wadsworth-Emmons reaction products **33a-c**, which were isolated after column chromatography and recrystallisation as shelf-stable solids in 34-50% yields (Scheme 1).



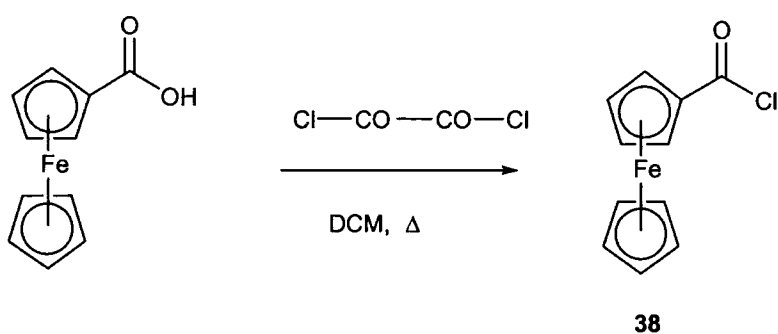
Scheme 1. Synthesis of Horner-Wadsworth-Emmons derivatives **33a-c**.

To obtain more highly functionalised derivatives of system **33**, we used the mono-methyl analogue **33c**, which by deprotonation with LDA in dry THF at -78°C , followed by *in situ* trapping of the lithiated species with methyl chloroformate gave the methyl ester derivative **36** (67% yield) which was reduced with lithium aluminium hydride to the corresponding hydroxymethyl derivative **37** (79%) (Scheme 2). This route followed precedents set with the anthracene-TTF system ^[2].

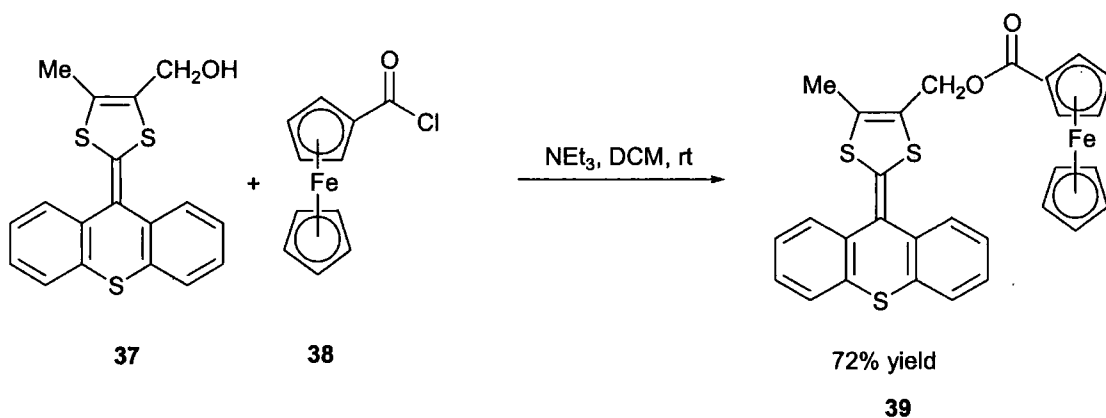


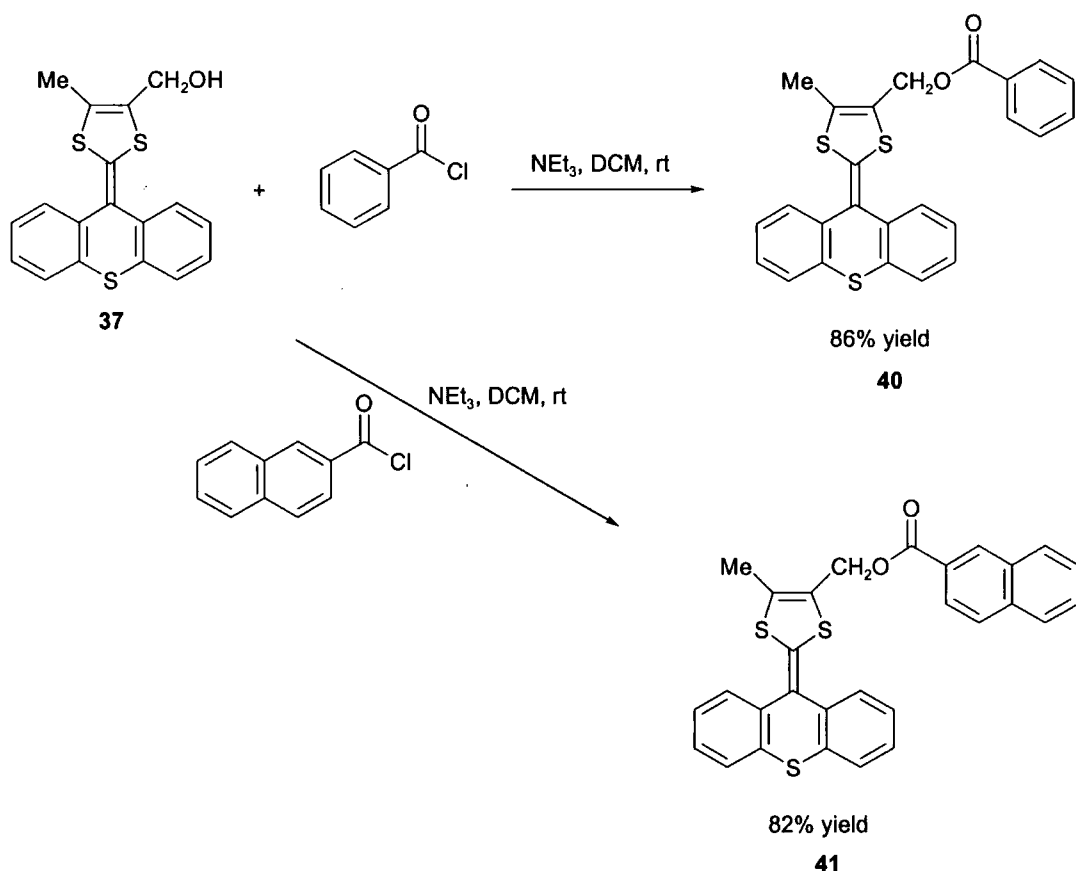
Scheme 2. Esterification followed by reduction of **33c**.

To utilise further the hydroxymethyl substituent of **37** in the synthesis of new derivatives, we decided to attach a ferrocenyl unit via an ester linkage, with the hope that the one-electron oxidation wave of the ferrocene might provide a redox marker to help us to study the electrochemistry of this system. For this purpose, ferrocene carbonyl chloride **38** ^[3] was prepared quantitatively from the corresponding carboxylic acid by heating under reflux with oxalyl chloride for several hours in dry dichloromethane (DCM).



The acid chloride **38** was then added at room temperature to a solution of compound **37** in dry DCM, containing triethylamine ^[3], to yield compound **39** which was isolated by column chromatography and then recrystallised from hexane, in 72% yield.

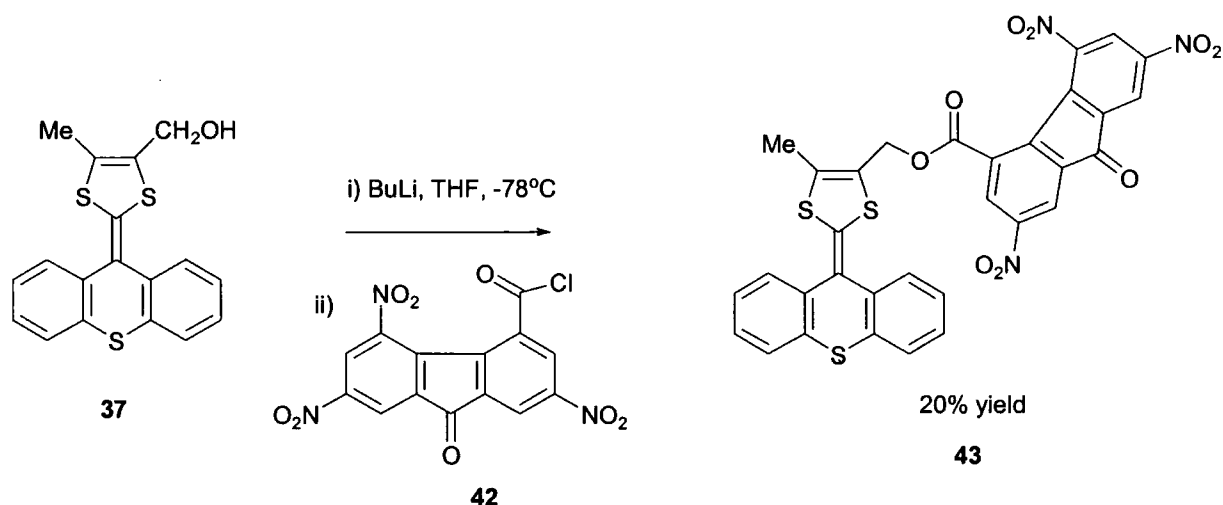




Scheme 3. Synthesis of benzoyl and 2-naphtoyl derivatives **40** and **41**.

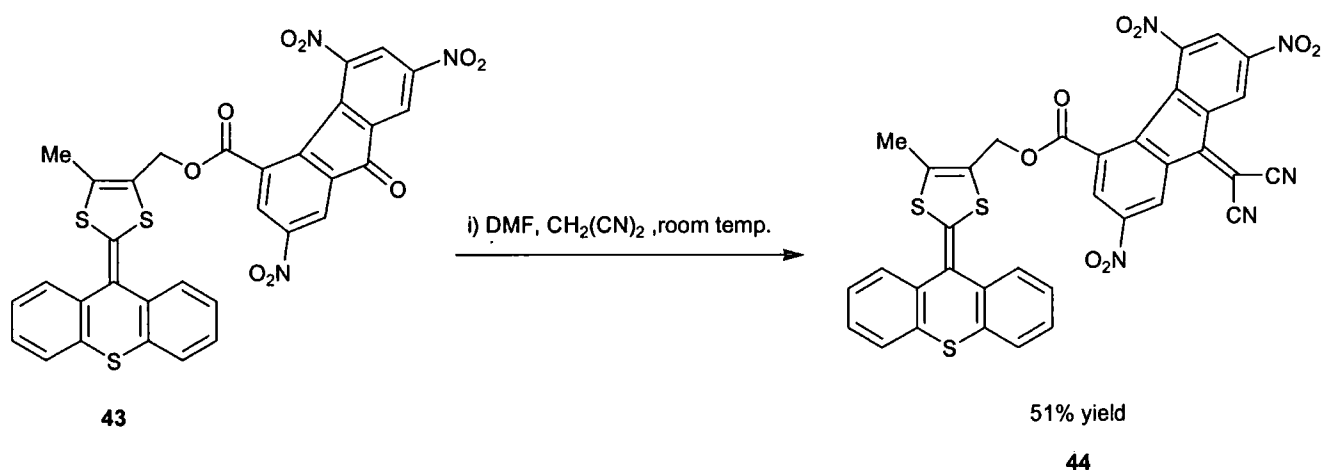
For the related ester compounds **40** and **41** the same protocol was used, starting with commercial benzoyl chloride and 2-naphtoyl chloride, respectively (Scheme 3).

The suitability of compound **37** for further elaboration was also established by reaction of its lithium alkoxide salt with 2,4,6-trinitro-4-(chlorocarbonyl)fluoren-9-one **42** ^[4, 5] to afford the donor- σ -acceptor compound **43** as black crystals in 20% yield (Scheme 4). This reaction was found to be very sensitive and any excess base, if present, would destroy the acid chloride.



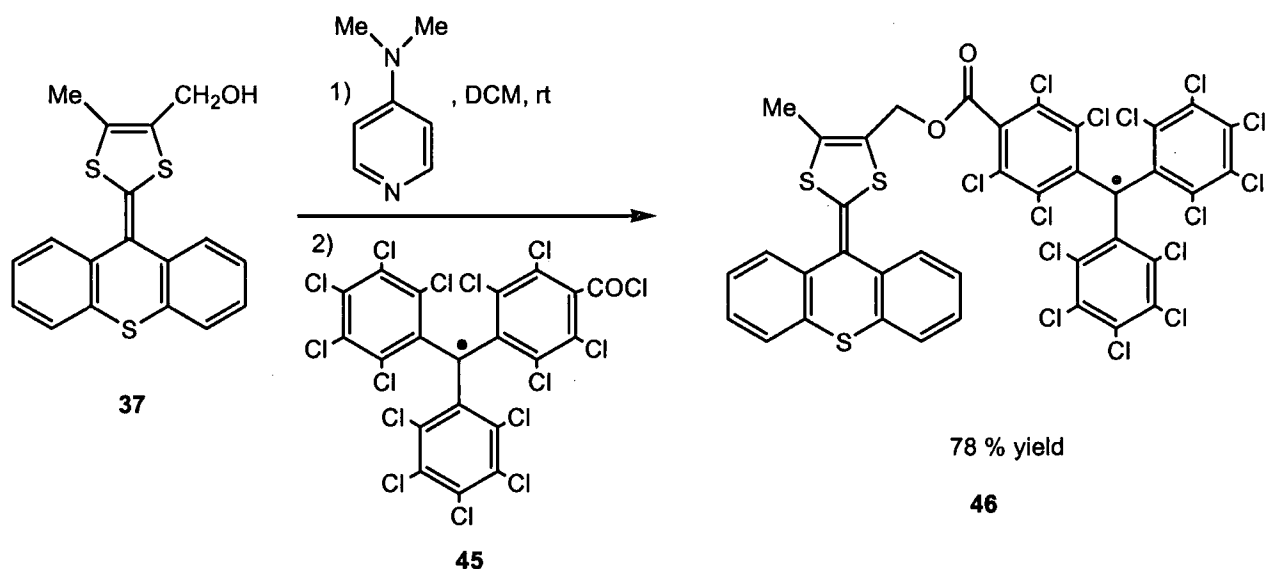
Scheme 4. Synthesis of the donor-acceptor complex **43**.

The electron acceptor ability of the fluorenone moiety in **43** was increased^[4, 5] by conversion to the dicyanomethylene derivative **44** by treatment with malononitrile in DMF solution (Scheme 5). Compound **44** was isolated as a dark green solid in 51% yield, and it is notable that this Knoevenagel reaction proceeded smoothly on such a highly-functionalised molecule as **43**.

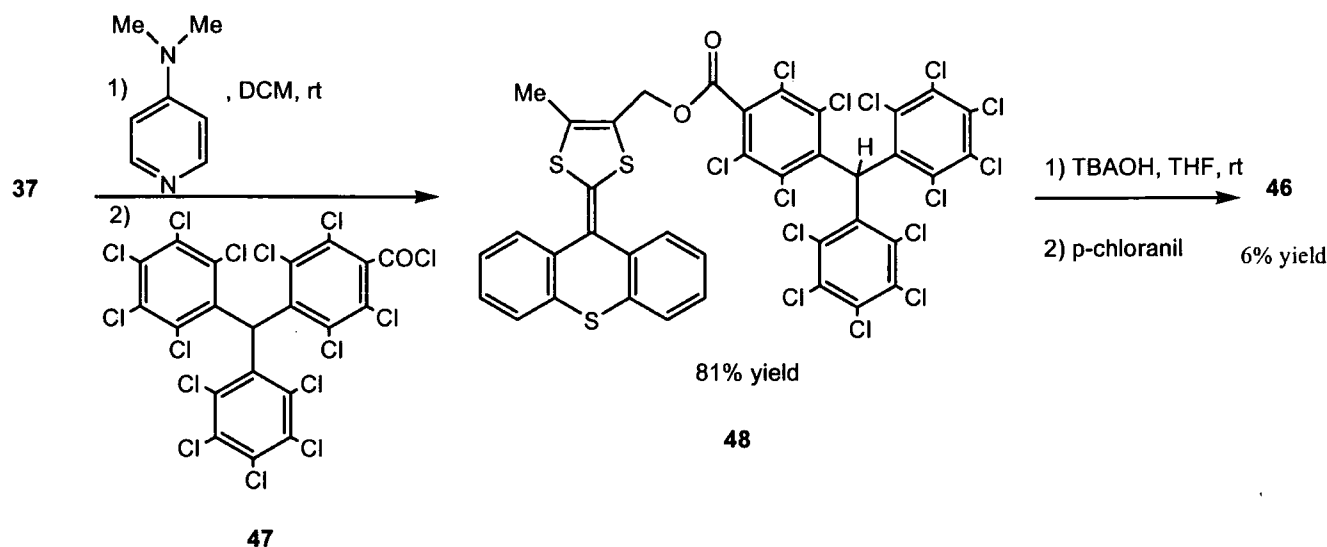


Scheme 5. Conversion of **43** to the dicyanomethylene derivative **44**.

Again with a view to attaching a redox marker to the 9-(1,3-dithiol-2-ylidene)thioxanthene system, reaction of **37** with 4-[bis(2,3,4,5,6-pentachlorophenyl)methyl]-2,3,5,6-tetrachlorobenzoyl chloride radical (PTM) **45** ^[6, 7] (obtained by treatment with thionyl chloride in DCM at room temperature of the corresponding benzoic acid derivative) was conducted in the presence of 4-(dimethylamino)pyridine to give the stable radical species **46** in 78% yield (Scheme 6). Compound **48** was similarly obtained in 81% yield by reaction of the hydroxymethyl derivative **37** with PTM acid chloride **47**, but the oxidation of **48** to the radical species **46** using tetrabutylammonium hydroxide followed by *p*-chloranil ^[8] was inefficient (only 6% yield) (Scheme 7). We assumed that the base was too strong and partially destroyed the ester functionality. Moreover, these radical species are not stable in solution in light; they undergo photolytic degradation, which required us to work in dark conditions.



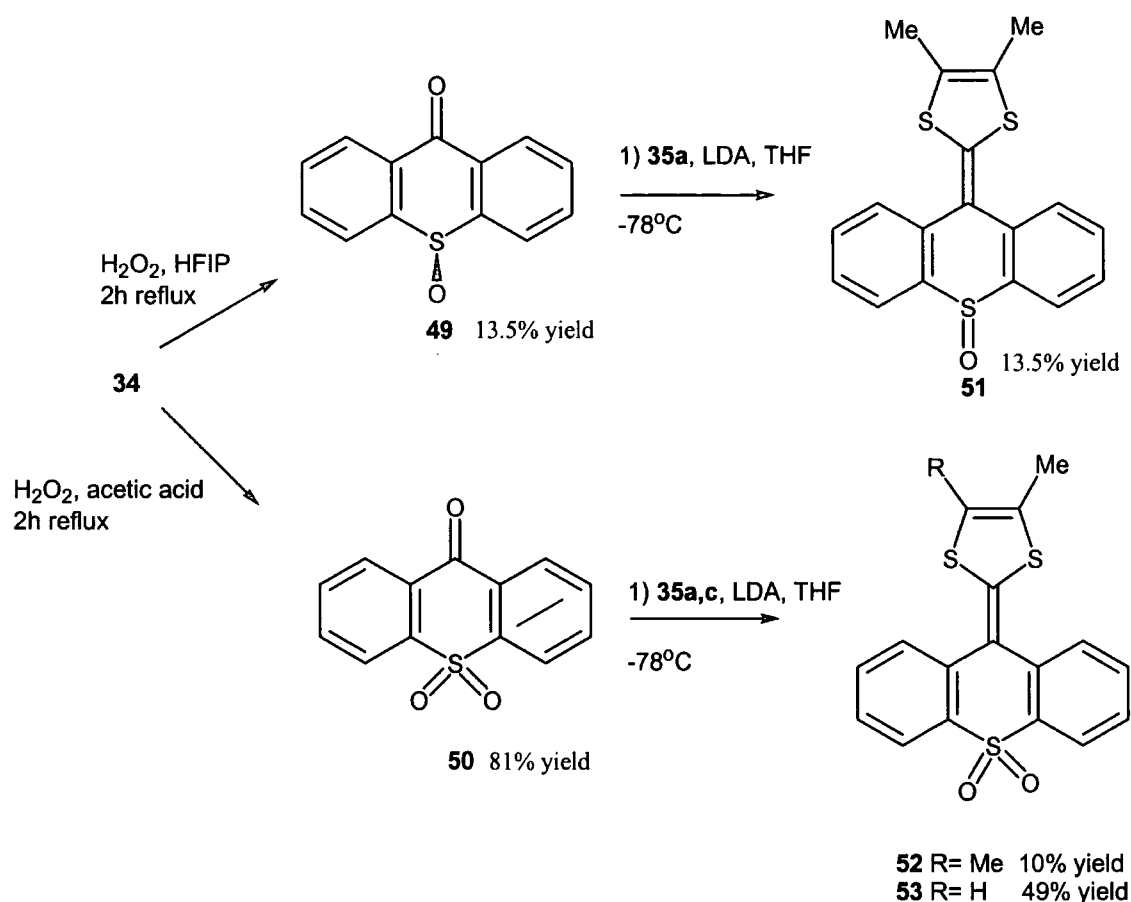
Scheme 6. Synthesis of the donor-acceptor complex **46**.



Scheme 7. Synthesis of the donor-acceptor complex **46** via a different route.

We also targeted the sulfoxide **51** and sulfone derivatives **52** and **53** to examine the effects of sulphur oxidation on the redox properties of the system. Thioxanthen-9-one **34** was oxidised to the sulfoxide derivative **49** (13.5% yield) or the sulfone **50** (81% yield) using hydrogen peroxide in hexafluoropropan-2-ol ^[9] or acetic acid ^[10], respectively (Scheme 8). Subsequent reactions of **49** and **50** with the appropriate phosphonate ester reagents **35a** or **35c** gave the products **51–53**.

The sulfoxide derivative **49** was very difficult to synthesise and we had many attempts using different oxidising reagents such as 3-chloroperoxybenzoic acid ^[11, 12] where a complex product mixture was obtained, and then sodium perborate tetrahydrate in acetic acid ^[13] or sodium metaperiodate where no reaction occurred and we recovered the starting material.



Scheme 8. Synthesis of sulfoxide and sulfone derivatives **51**, **52** and **53**.

Compound **52** crystallises as a $52 \cdot \frac{1}{2} \text{C}_4\text{H}_8\text{O}_2$ solvate, in which the ethyl acetate molecule is disordered between two (overlapping) positions, related via an inversion centre. Molecules **33a** and **52** show saddle-like distortions, similar to those observed in anthracene-TTF systems ^[14]. The thioxanthene moiety is folded along the C(9)...S(1) vector, with a small additional twisting distortion. Thus, benzene rings *A* and *B* are planar and form a dihedral angle of 144.9° (**33a**) and 137.9° (**52**); the S(1) and C(9) atoms are practically coplanar with ring *B* but are displaced from the plane of *A* in opposite directions, respectively by 0.10 and −0.13 Å in **33a**, and by 0.18 and −0.07 Å in **52**.

The distortion is probably caused by steric repulsion between the S(2) and S(3) atoms and the *peri* H atoms, since the thioxanthene system is planar in both

thioxanthone-10,10-dioxide ^[15] and 1-thioxanthenylidene-1H-cyclopropa(b)naphthalene ^[16], which are free from such overcrowding. The dithiole ring is slightly folded along the S(2)...S(3) vector, by 7.9° in **33a** and 8.4° in **52**. The C₂C(9)=C(14)S₂ moiety in **33a** is substantially non-planar: the S(2)C(14)S(3) and C(10)C(9)C(13) planes form dihedral angles of 10.0° (**33a**) and 6.7° (**52**). However, in **33a** this non-planarity is mainly due to a twist around the C(9)=C(14) bond: the torsion angle between the directions of the *p*π orbitals of C(9) and C(14) [*p*π-C(9)-C(14)-*p*π] equals 6.5°. In **52** the twist is negligible, and the distortion is essentially boat-like.

Thus the oxidation of the S(1) atom slightly enhances the folding of the thioxanthene moiety, although it does not affect the lengths of either the S(1)-C bonds [average 1.758(2) in **33a**, and 1.754(1) Å in **52**] or the C-C bonds in this moiety significantly.

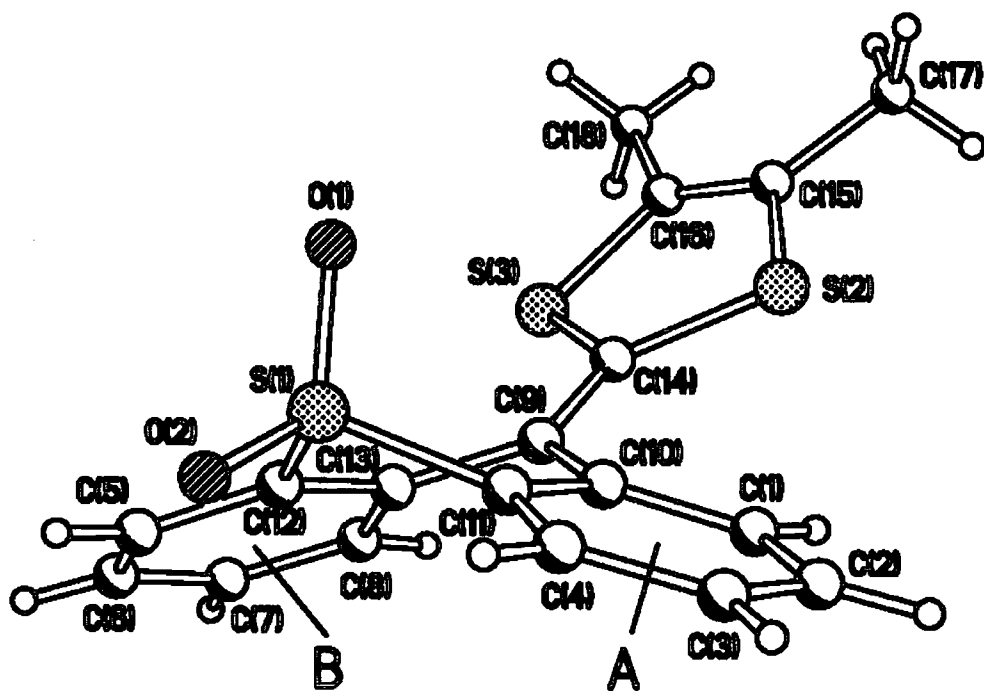
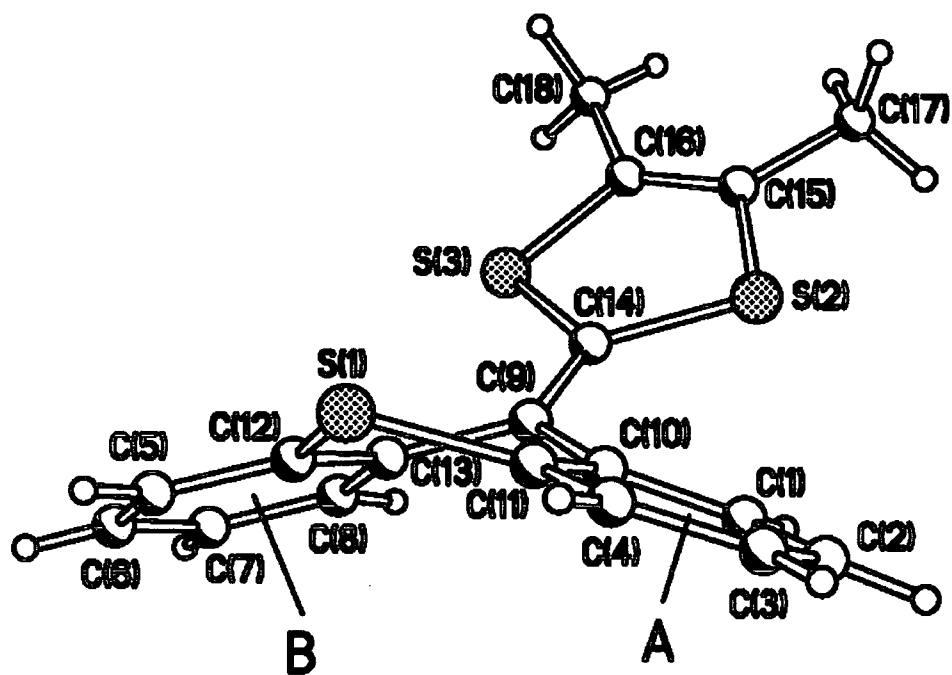


Figure 2. Molecular structures of 33a (top) and 52 (bottom) determined by single crystal X-ray analysis.

2) Electrochemical and spectroscopic studies

The electrochemistry of system **33** has been studied by cyclic voltammetry (CV) to determine its redox potential and the number of electrons involved during its oxidation. A point of particular interest was to establish if oxidation would afford a detectable radical cation species (like in system **25a**)^[17] or whether a single, two-electron process would occur (like in anthracene-TTF **8**) to give a dication^[2]. The data for compounds **33a-c**, **36**, **37**, **40** and **41** are presented in Table 1. One general trend is immediately apparent, and it is consistent with that observed previously for TTF^[18] and anthracene-TTF derivatives^[19], namely, that the attachment of an electron-withdrawing ester substituent results in a positive shift of the redox wave (i.e. the system becomes more difficult to oxidise). Thus the E_{pa}^{ox} values for compounds **36**, **40** and **41** are shifted by + (0.15 to 0.17 V) compared to compound **33c**. It is also known in the TTF series that attachment of alkylthio groups raises the oxidation potential^[20] so the higher oxidation potential of **33b** compared to **33a** and **33c** was predictable. It was, however, unexpected that compound **33c** (with one CH₃ substituent) would be easier to oxidise (by 100 mV) than its dimethyl analogue **33a**.

Compound	E_{pa}^{ox}/V	E_{pc}^{red}/V	λ/nm ($\epsilon/dm^3 mol^{-1} cm^{-1}$)
33a	0.77	0.61	384 (12.76x10 ³)
33b	0.90	0.70	377 (10.5x10 ³)
33c	0.67	0.63	378 (12.16x10 ³)
36	0.83	0.72	368 (15.4x10 ³)
37	0.66	0.60	376 (10.46x10 ³)
40	0.82	0.78	374 (81.15x10 ³)
41	0.84	0.78	375 (85.78.10 ³)

Table 1. Cyclic voltammetric data and UV-vis spectroscopic data for **33a-c**, **36**, **37**, **40**, **41**.

^a E_{pa}^{ox} is the oxidation peak potential on the first anodic scan; E_{pc}^{red} is the coupled reduction peak potential on the cathodic scan.

[Experimental conditions: acetonitrile, Pt electrode, versus Ag/AgCl, electrolyte $Bu_4N^+BF_4^-$ (0.1 M), 20 °C, scan rate 100 mV/s.]

The cyclic voltammograms of compounds **33c**, **36** and **37** (Figure 3) were recorded in acetonitrile under the conditions stated in Table 1.

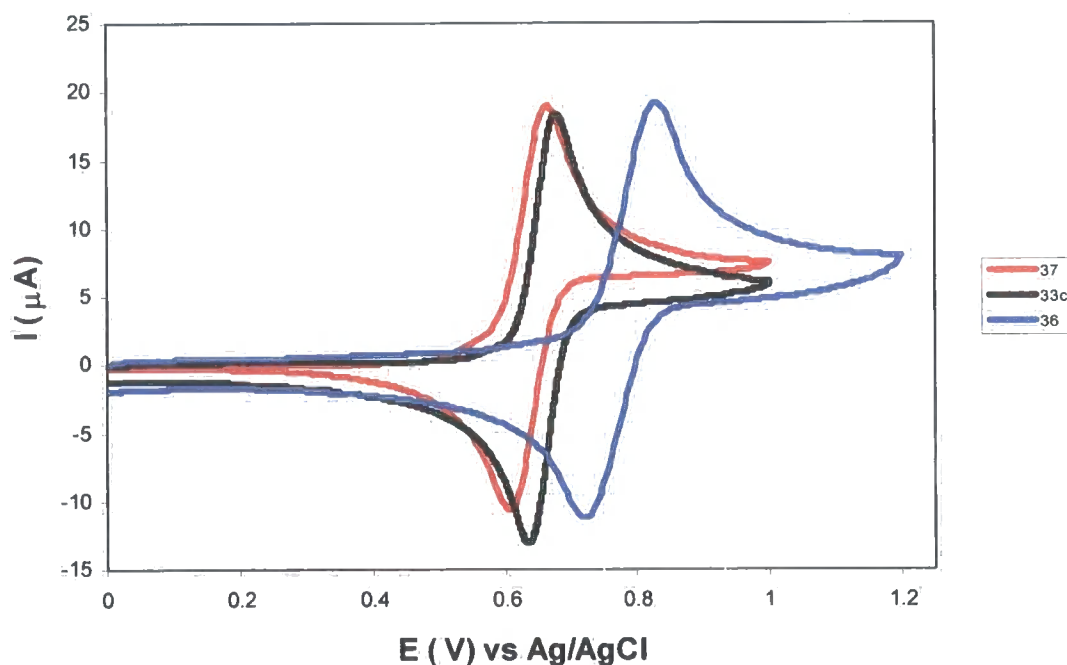


Figure 3. Cyclic voltammograms of compounds **33c**, **36** and **37**.

As can be seen from Figure 3 we observed a single, quasi-reversible oxidation wave. The quasi-reversibility can be explained by a gain of aromaticity at the oxidised stage (as with anthracene-TTF) **8** that is then lost upon reduction back to the neutral species. However, this delay in observing the coupled reduction peak cannot confidently be attributed to a change of conformation between the oxidised form and the neutral one,

which is the case for anthracene-TTF derivatives, where the difference between the values of E_{pa}^{ox} and E_{pc}^{ox} is much larger (ca 0.35 V). The behaviour of compounds **33c**, **36** and **37** was essentially unchanged (± 10 mV for the values of the peak potentials) when several experimental parameters were varied independently in the CV experiments, namely, the solvent (acetonitrile, THF, DCM), the electrolyte ($Bu_4N^+BF_4^-$, $Bu_4N^+PF_6^-$, $Bu_4N^+ClO_4^-$), the temperature (0-20°C) and the scan rate (10-1000 mV/s). In particular, lowering the temperature to 0 °C had no effect on the reduction potential of the dication of **33a**. This is in contrast to data for anthracene-TTF derivatives, e.g. **9** [21], for which the reduction potential is shifted to significantly lower potentials as the temperature is lowered, due to the conformational change accompanying this process being disfavoured.

Based on the data in Table 1 and Figure 3 it was not possible to establish the number of electrons involved in the redox process.

The electrochemistry of ferrocene being well known as a reversible single-electron process arising from the Fe^{2+}/Fe^{3+} couple, we had covalently attached a ferrocenyl unit to compound **37**, to obtain **39** as discussed above, hoping that by comparison of the current passed in the waves for compound **39** we could determine the number of electrons involved in the oxidation process of system **33**. The CV of compound **39** is shown in Figure 4. Unfortunately, the waves from the ferrocenyl and thioxanthene moieties overlapped, due to the ester substituent directly attached to the ferrocene raising the potential of the Fc^0/Fc^+ couple: the separation was improved at low temperature but not to the extent that any conclusions could be drawn.

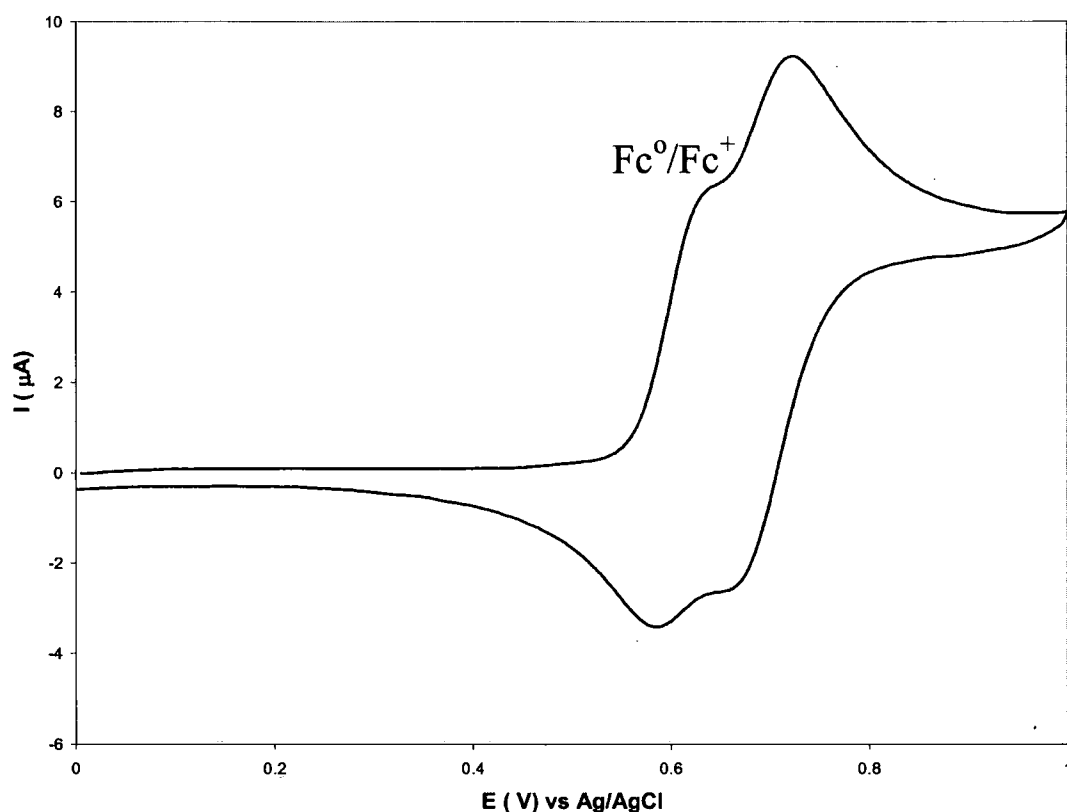


Figure 4. Cyclic voltammetry of **39** in DCM, containing tetrabutylammonium tetrafluoroborate as electrolyte (0.1 M), at 20° C, with Ag/AgCl as the reference electrode.

Thus, for the same purpose, we attached a very different marker group, for which the redox potentials would be considerably more negatively shifted, namely the polynitrofluorenone **42**. We had previously established that this π -electron acceptor system possesses three, one-electron reduction waves, all of which are fully reversible [4, 5].

The CV of compound **43** was recorded with added ferrocene as an internal reference (Figure 5). (Note that unlike compound **39** the wave from the unsubstituted ferrocene unit is clearly separated from the thioxanthene wave).

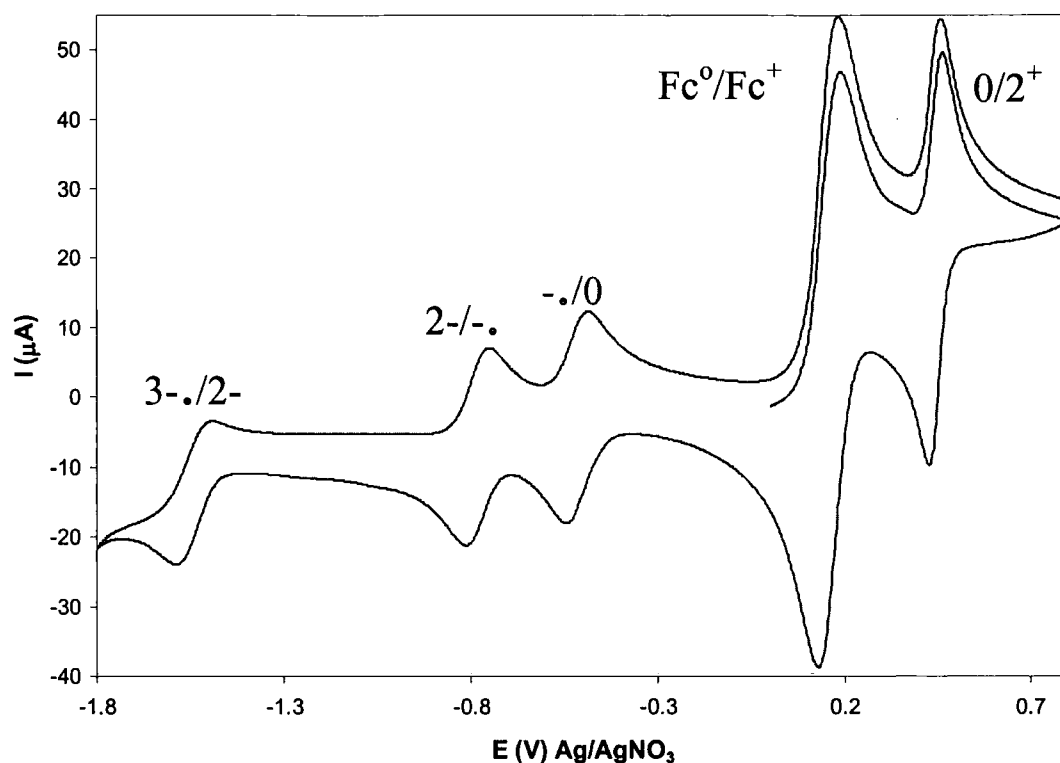


Figure 5. Cyclic voltammetry of **43** in the presence of added ferrocene as internal reference showing the redox process associated with each wave. Solvent DCM, containing tetrabutylammonium tetrafluoroborate as electrolyte (0.1 M), at 20° C, with Ag/Ag(NO₃) as the reference electrode.

Now we can observe the three clean one-electron reduction waves of the polynitrofluorenone unit of **43** ($E^{1/2}$ -1.54, -0.78 and -0.51 V) and the single oxidation wave of the (1,3-dithiol-2-ylidene)thioxanthene moiety (E_{pc}^{ox} +0.44 V) with ca. twice the current associated with this wave, which clearly shows that system **33** is oxidised to the dication species in a single, two-electron wave as for anthracene-TTF.

The UV/vis spectra of **33a-c**, **36**, **37** (Figure 6) have been recorded in chloroform, and they all show a maximum of absorbance between 368 nm and 384 nm attributed to the absorbance of the 9-(1,3-dithiol-2-ylidene)thioxanthene moiety, the shortest wavelength corresponding to the ester derivative **36**, which is not really explicable.

In the TTF series, there is a logical progression in spectroscopic absorption behaviour (i.e. λ_{max} for TTF-CO₂R derivatives are red shifted by 64 nm compared to TTF) ^[22] which is readily explained by extension of conjugation involving the carbonyl part of the ester group.



On the contrary, compound **36** behaves similarly to TTF-anthraquinone derivatives (i.e. λ_{max} for TTFAQ-CO₂R derivatives are blue shifted by 2 nm compared to TTFAQ) and trimethyl-TTF derivatives (i.e. λ_{max} for TriMe-TTF-CO₂R derivatives are blue shifted by 52 nm compared to TriMe-TTF) but unfortunately no consistent reasons have been established ^[23, 24]. We observed an additional shoulder for **36** at 430 nm, suggesting the presence of intramolecular charge transfer within the molecule due to the conjugated electron withdrawing ester group.

For compound **41** we also observed the absorbance of the naphthoyl substituent at 339 nm.

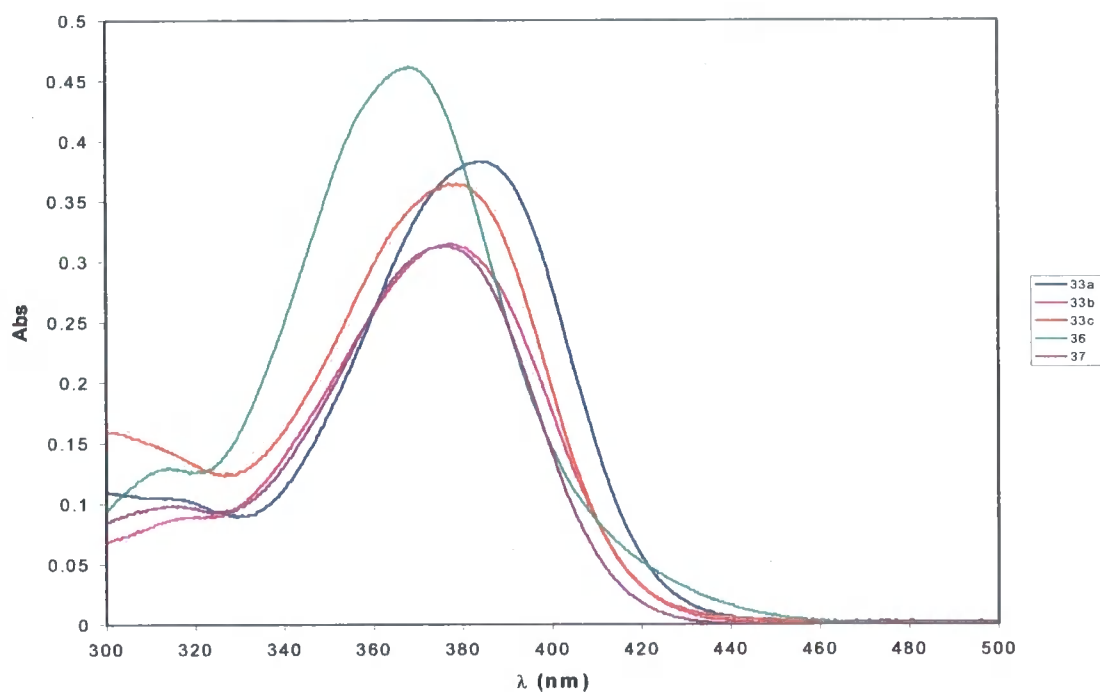


Figure 6. UV/vis absorption spectra of derivatives **33a-c**, **36**, **37**.

The UV/vis spectroscopic study of **43** reveals a maximum of absorbance at 361 nm [Figure 7(a)], and the presence of charge transfer bands between 560-800 nm observable at low concentration [Figure 7(b)], confirming the intramolecular interactions along the molecule between the acceptor and the donor parts.

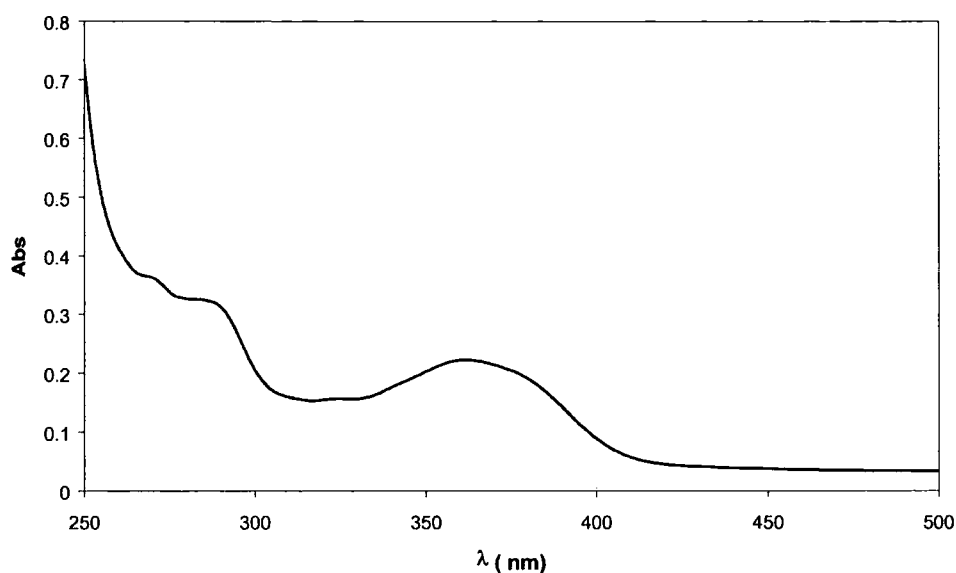
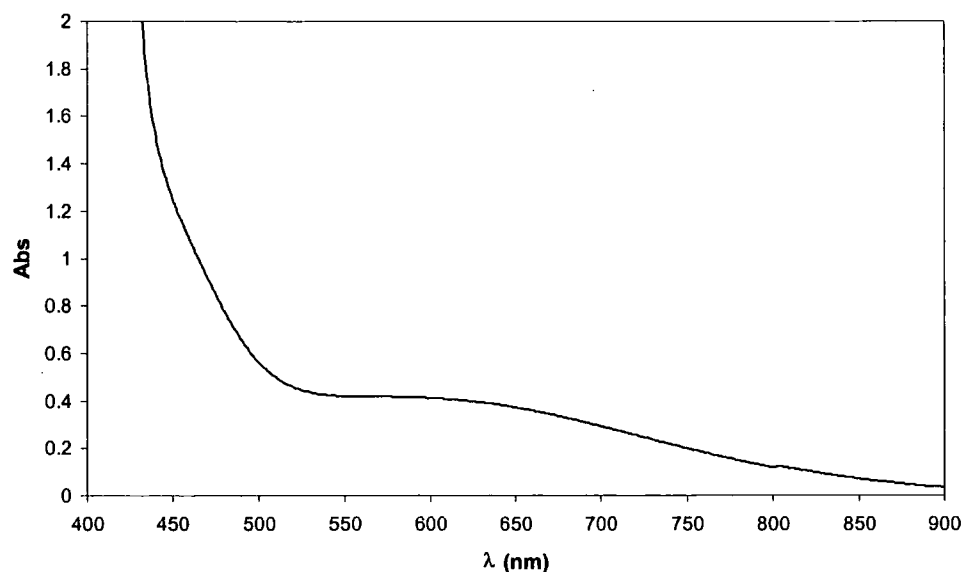


Figure 7. (a) UV/vis absorption spectrum of **43** in CHCl_3 solution.



(b) Charge transfer band of **43**, $[c] = 37.46 \times 10^{-3} \text{ mol/L}$.

The cyclic voltammetry of **44** (Figure 8) also similarly confirmed a single two-electron process for system **33**. A UV/vis/nearIR spectroscopic study on **44** showed a maximum absorbance at 374 nm and also intramolecular charge transfer bands (Figure 9), with a red shift for the HOMO-LUMO transition (700-1000 nm) compared to **43**, due to the dicyanomethylene group enhancing the electron acceptor ability.

The existence of charge transfer in compound **44** in the solid state is also manifested in a lowering of the frequency of the $C\equiv N$ stretching band in the IR spectrum compared with a neutral analogue as seen in other 9-dicyanomethylenefluorene systems ^[4].

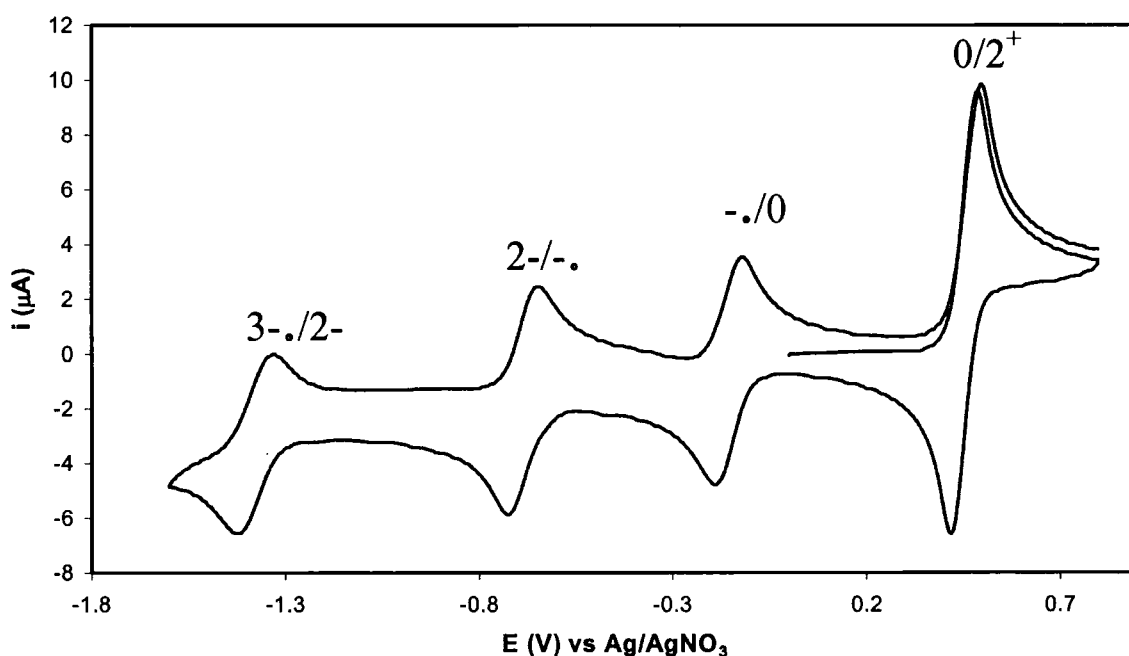


Figure 8. Cyclic voltammetry of **44** in DCM, containing tetrabutylammonium tetrafluoroborate as electrolyte (0.1 M), at 20° C, with Ag/Ag(NO₃) as the reference electrode.

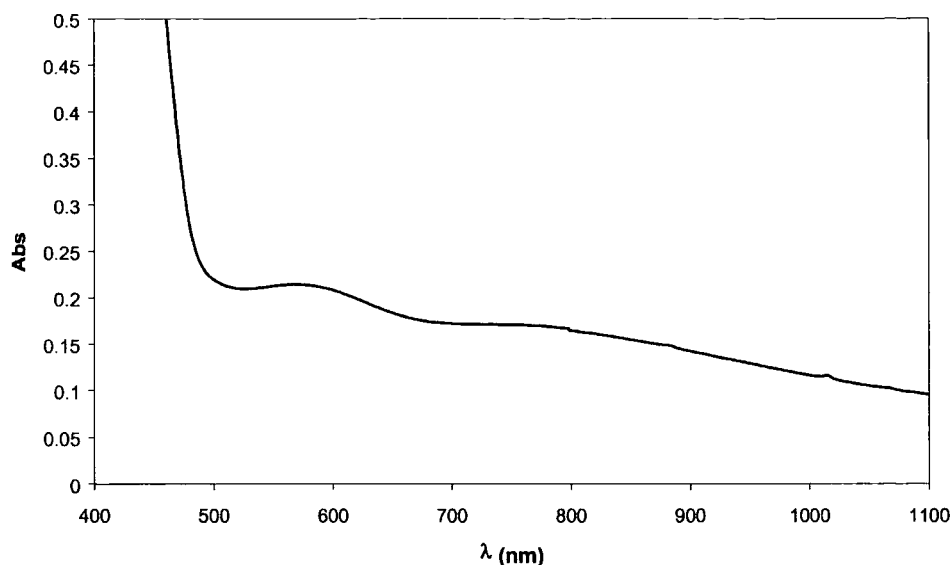


Figure 9. Charge transfer bands of **44**, $[c]=18.29\text{E-}3$ mol/L.

CV data for compound **46** were, however, inconclusive. It is known that the electrochemistry of the PTM unit **45** occurs as a single-electron, reversible, reduction wave, but unfortunately the cyclic voltammetry of **46** served only to establish that both donor and acceptor species were present in the molecule (Figure 10). Indeed the intensity of the both waves is not consistent with the known structure **46**, possibly due to a problem of diffusion of the molecule to and from the electrode under electrochemical bias.

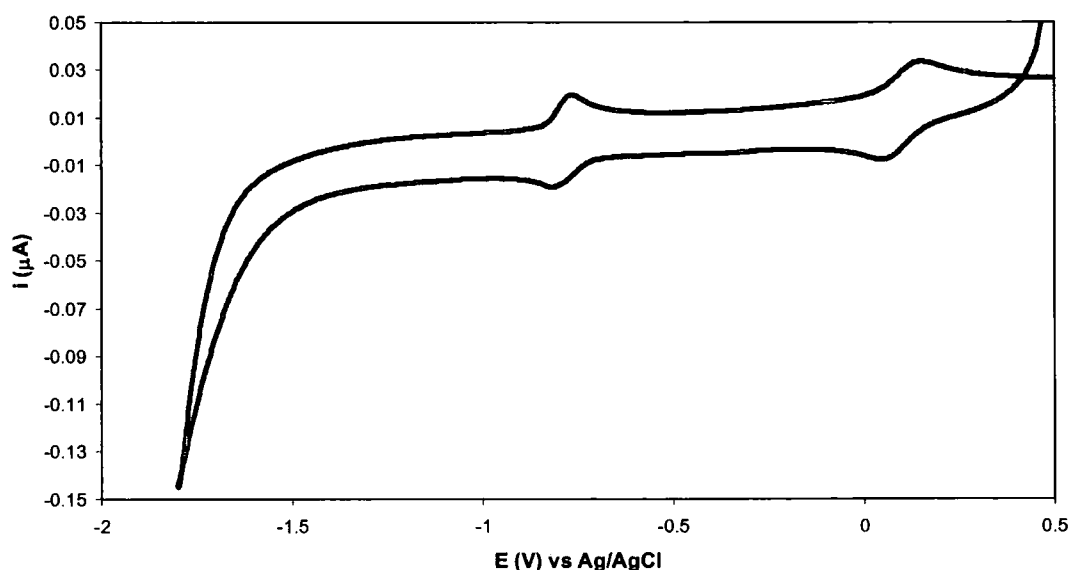


Figure 10. Cyclic voltammetry of **46** in DCM, $\text{Bu}_4\text{N}^+\text{BF}_4^-$ (0.1 M) as electrolyte.

The UV/Vis spectrum of **46** shows absorbances at λ_{max} 383 nm for the donor moiety, and three characteristic bands at λ_{max} 283, 368 and 500-560 nm for the PTM unit.

We also characterised this radical by Electron Spin Resonance (EPR) spectroscopy. The EPR spectrum of the radical **46** was recorded in a solution of 0.2 M of $\text{Bu}_4\text{N}^+\text{PF}_6^-$ in DCM (Figure 11). The symmetry of the signal indicates the presence of only one radical species in solution. The amplification of this signal reveals the existence of many other signals; they are caused by the presence of the natural abundance of ^{13}C in the molecule. We have characterised this radical by the following parameters:

Hyperfine coupling constants: $a_\alpha = 29.60$ G; $a_p = 12.78$ G; $a_o = 10.60$ G; g-factor = 2.0022 line width = 1 G. The value of the g-factor is characteristic of other PTM derivatives ^[8, 25] so we can confidently assign this signal to compound **46**.

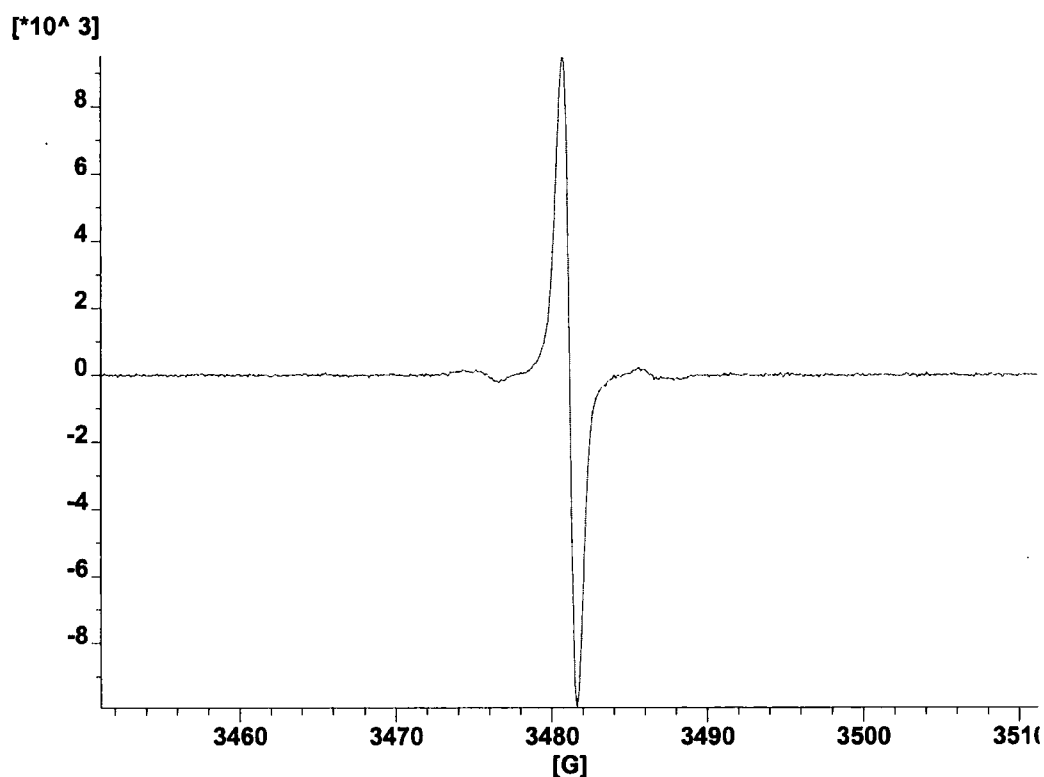


Figure 11. Simulated EPR spectrum of **46** in DCM solution.

We have also studied the electrochemistry of the sulfoxide **51** and sulfone **52** to examine the effect of sulfur oxidation on the redox properties of this system. We postulated that for these derivatives the radical cation species might be observable, due to the fact that the polarity of the S–O bond(s) would make removal of the second electron more difficult. Indeed, the cyclic voltammetry of these compounds (Figure 12) recorded in THF, revealed two oxidation waves (presumably both are single-electron processes) the second one being irreversible for both compounds. It is notable that compared to the parent system **33a**, the first oxidation potential is positively shifted, although the potentials for both **51** (E^{ox} 1.06 V) and **52** (E^{ox} 1.08 V) are very similar, whereas the second wave (radical cation/dication) is positively shifted by 210 mV for the sulfone (E^{ox} 1.61 V) compared to the sulfoxide (E^{ox} 1.40 V).

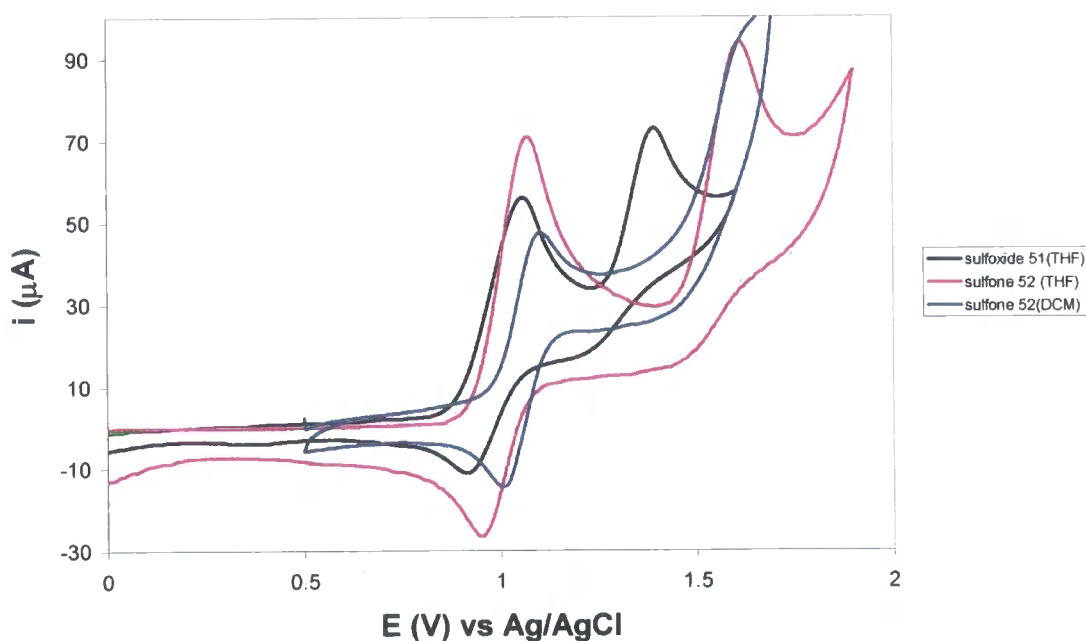


Figure 12. Cyclic voltammetry of **51** and **52** in THF, containing tetrabutylammonium tetrafluoroborate as electrolyte (0.1 M), at 20° C, with Ag/AgCl as the reference electrode.

However, cyclic voltammetry of sulfone **52** under similar conditions in DCM, showed only a single quasi-reversible wave at E^{ox} 1.11 V. This represents a marked solvent dependency for the redox processes for **52**. We have not determined whether this

wave corresponds to a one or two-electron process. However, it seems inconceivable that the second wave observed in THF shifts negatively by ca. 400 mV in DCM to overlap the first wave. Therefore, we believe that the wave in THF is a one-electron process and the dication is not observed in DCM.

Further confirmation that the radical cation of sulfone **52** was generated in the CV was provided by simultaneous electrochemistry and epr experiments. The epr spectrum of **52** was recorded in a solution of 0.2 M Bu₄NPF₆ in DCM (Figure 13) initially at $E = 0.5$ V, where no signal appeared, and then at $E = 1.04$ V. Under these conditions of higher applied potential we observed an intense signal with extensive fine structure. The simulation of this spectrum showed that the spin distribution is delocalised over the whole molecule, i.e. **52**^{•+} should be viewed as a π -extended system. The spectrum is very symmetrical which is diagnostic of only one radical species present in solution.

We cannot assign any proton coupling but we can characterise this radical as follows: g-factor = 2.0059; line width = 0.2 Gauss; Lorentzian/Gaussian = 1. These data are similar to those known for TTF^{•+} derivatives^[26].

We observed that the concentration of the radical decreased gradually with time, which could be due (i) to further oxidation of the cation radical to the dication species, (ii) disproportionation to dication and neutral species (both would be epr silent) or (iii) some other decomposition pathway.

Attempts at chemical oxidation of **52** in DCM using trifluoroacetic acid did not give any epr signal, and according to the UV/vis spectrum of this solution, which remained unchanged, this acid was not strong enough to oxidise this compound.

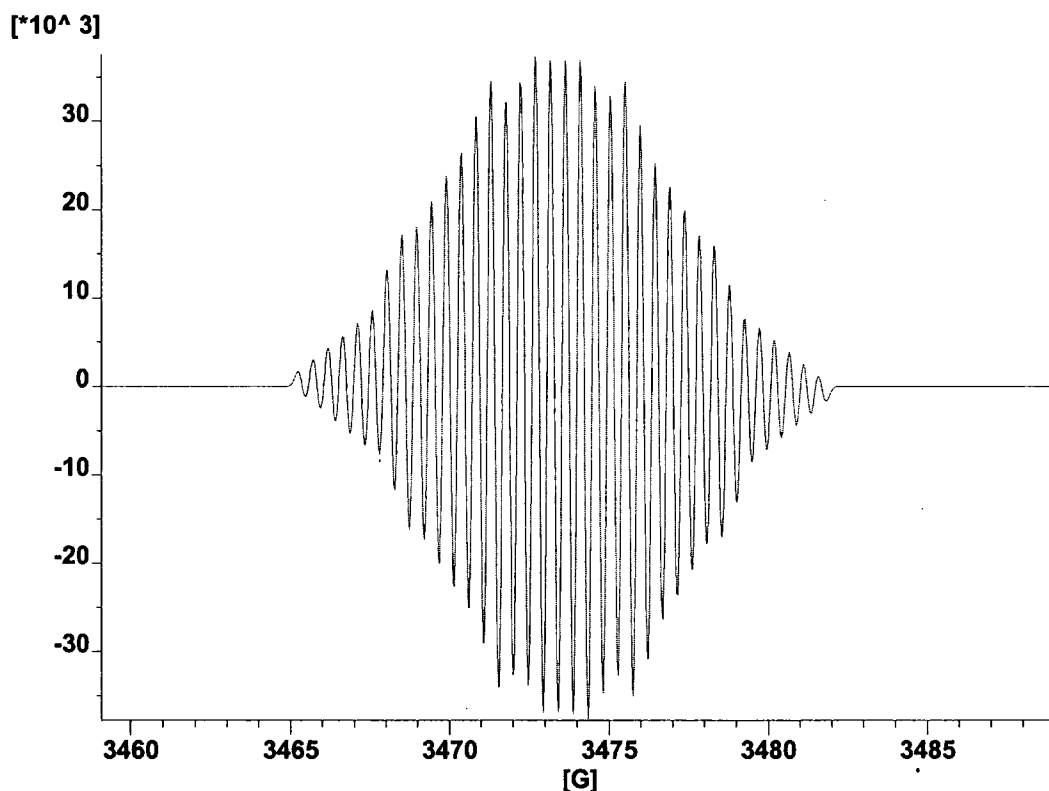


Figure 13. Simulated epr spectrum of $52^{+\bullet}$ generated upon electrolysis of **52** in DCM.

3) Theoretical calculations and electrocrystallisation experiments

With the aim of gaining a deeper understanding of the electrochemical and structural properties of the 9-(1,3-dithiol-2-ylidene)thioxanthene system **33** in the neutral and oxidised states, density functional theory (DFT) calculations were performed by Professor Ortí's group at the University of Valencia, and these results are summarised below. The calculations assume a C_{2v} planar structure and a butterfly-shaped C_s structure. The calculated minimum energy conformation for the neutral species shows a folding angle of 138.3° between the wings of the butterfly, which is very close to value of 144.9° determined experimentally by X-ray analysis of **33a** (Figure 14). This slight difference can be explained by the fact that calculations overestimate the folding of the molecule because they are performed on one isolated molecule, whereas in the crystal, packing forces tend to reduce the folding to achieve the most compact packing.

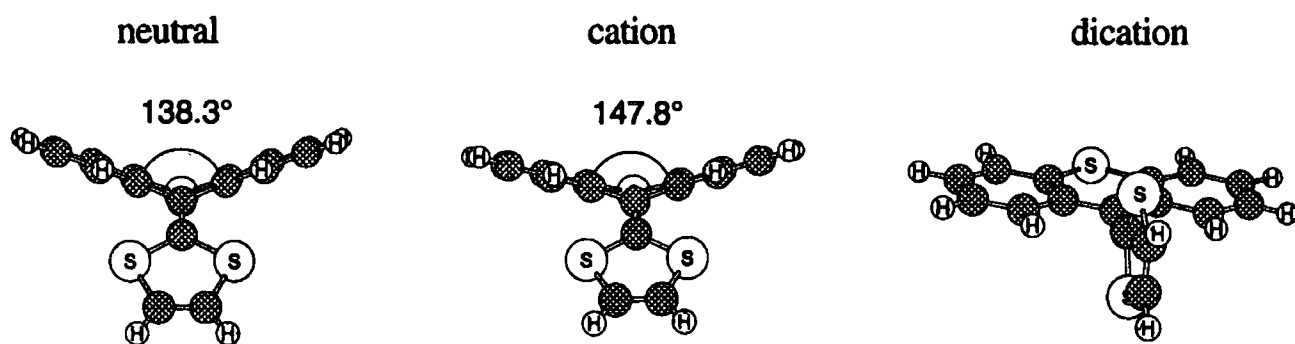


Figure 14. Calculated structures for neutral, cation radical and dication.

The calculations show that the cation radical keeps this distorted shape, but is slightly less folded (147.8°). The geometrical structure and the charge distribution calculated for this cation radical suggest that the charge is extracted from both the dithiole ring and the thioxanthene moiety (0.43 e removed from the dithiole ring and 0.57 e from the thioxanthene unit). The extraction of the second electron, still occurring from both parts of the molecule, to form the dication produces planarisation of the thioxanthenium unit while the dithiolium cation ring lies perpendicularly to the molecular plane, thereby avoiding steric interactions of the sulfur atoms with the *peri* hydrogens. In contrast to the monocation radical, the dication of **33** consists of two singly charged aromatic units: viz. 6π dithiolium and 14π thioxanthenium rings. Thus, based on aromaticity considerations for the molecule, it is entirely reasonable that the first and second oxidation processes of **33** should be very close in the potential scale, or even fuse into a single two-electron wave, as we observe experimentally.

These theoretical calculations are, therefore, in close agreement with the experimental results. The calculated structure of the neutral form is very close to the crystal structure determined by X-ray analysis. Unfortunately, all attempts to crystallise a dication salt for X-ray analysis by chemical oxidation with iodine or by electrocrystallisation have proved unsuccessful. Many attempts were made using compound **33a**, in different solvents, electrolytes and using different types of electrodes, but only powders or very thin hair-like microcrystals have been obtained (Table 2).

Similar attempts using the sulfone derivative **52**, varying the same parameters, also did not lead to the growth of any crystalline salts suitable for X-ray analysis (Table 3).

Solvent	Electrolyte	Fix E	Current	Temp.	Electrode	Time	Result
DCM	Et ₄ NBF ₄		1-3μA	RT	Thick	10 days	No oxidation
DCM	Bu ₄ NPF ₆		1-3μA	RT	Thick	10 days	Dication solution
DCM	Bu ₄ NPF ₆		2μA	8°C	Thin	11 days	No oxidation
DCM	Bu ₄ NCIO ₄		2μA	8°C	Thin	11 days	Dication +residue
DCM	Bu ₄ NAuI ₂		2μA	8°C	Thin	7 days	Decomposition
THF	Bu ₄ NPF ₆		1-3μA	RT	Thick	12 days	Partial oxidation
THF	Et ₄ NBF ₄		1-3μA	RT	Thick	12 days	Partial oxidation
chloroben zene	Bu ₄ NPF ₆	30.7V	0.8μA	RT	Thick	6 days	Decomposition
chloroben zene	Bu ₄ NCIO ₄	30.7V	0.8μA	RT	Thick	8 days	No oxidation
chloroben zene	Bu ₄ NAuI ₂	30.7V	0.8μA	RT	Thick	8 days	No oxidation

Table 2. Electrocrystallisation experiments performed on **33a**.

Solvent	electrolyte	Fix potential	Current	Temperature	Electrode	Time	Result
DCM	Bu ₄ NPF ₆		1-3μA	RT	Thin	7 days	No oxidation
DCM	Et ₄ NBF ₄		1-3μA	RT	Thin	7 days	No oxidation
THF	Bu ₄ NPF ₆		1-3μA	RT	Thin	12 days	No oxidation
DCM	Bu ₄ NPF ₆	8.8V	2 μA	8°C	Thick	10 days	No oxidation
DCM	Bu ₄ NClO ₄	8.8V	2 μA	RT	Thick	6 days	No oxidation
DCM	Bu ₄ NAuI ₂	8.8V	2 μA	RT	Thin	6 days	Partial oxidation

Table 3. Electrocrystallisation experiments performed on **52**.

4) Spectroelectrochemistry

The dication salt resulting from the oxidation of compound **33a** has been isolated by bulk electrolysis. The spectroscopic study of this species was carried out in acetonitrile (high solubility) and in dichloromethane (very low solubility) (Figure 15). The dication is characterised by two absorption bands (λ_{max} ~320 nm, ~440 nm) in both solvents, with a longer wavelength (red shift) for the second band in DCM possibly due to the formation of dimers.

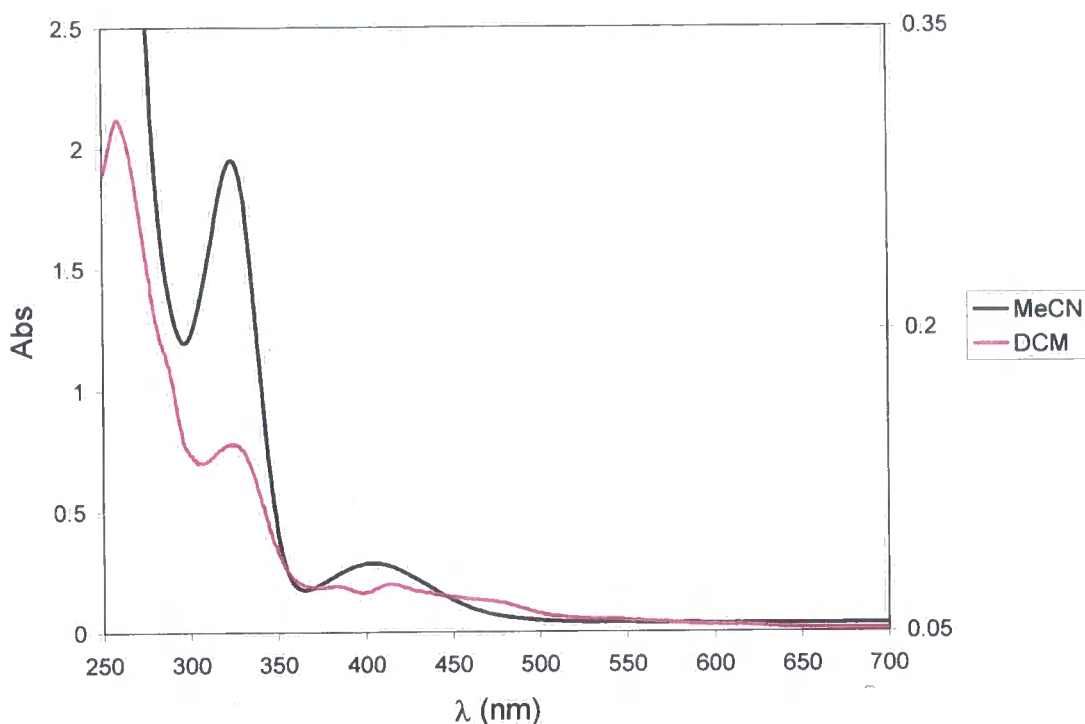


Figure 15. UV/vis absorption spectra of **33a** dication bis(perchlorate) salt.

The spectroelectrochemistry of **33a** has been studied in acetonitrile containing tetrabutylammonium hexafluorophosphate as electrolyte (0.2 M) (Figure 16). We observe the progressive oxidation of the neutral form to the dication species; upon reduction of the dication to the neutral species, the original spectrum is completely recovered. Both spectra show two isosbestic points confirming the electrolysis of only two species in solution, namely, the neutral form and the dication salt. We have also noticed that the dication salt is unstable in the presence of oxygen, and it tends to decompose back to the starting ketone **34**.

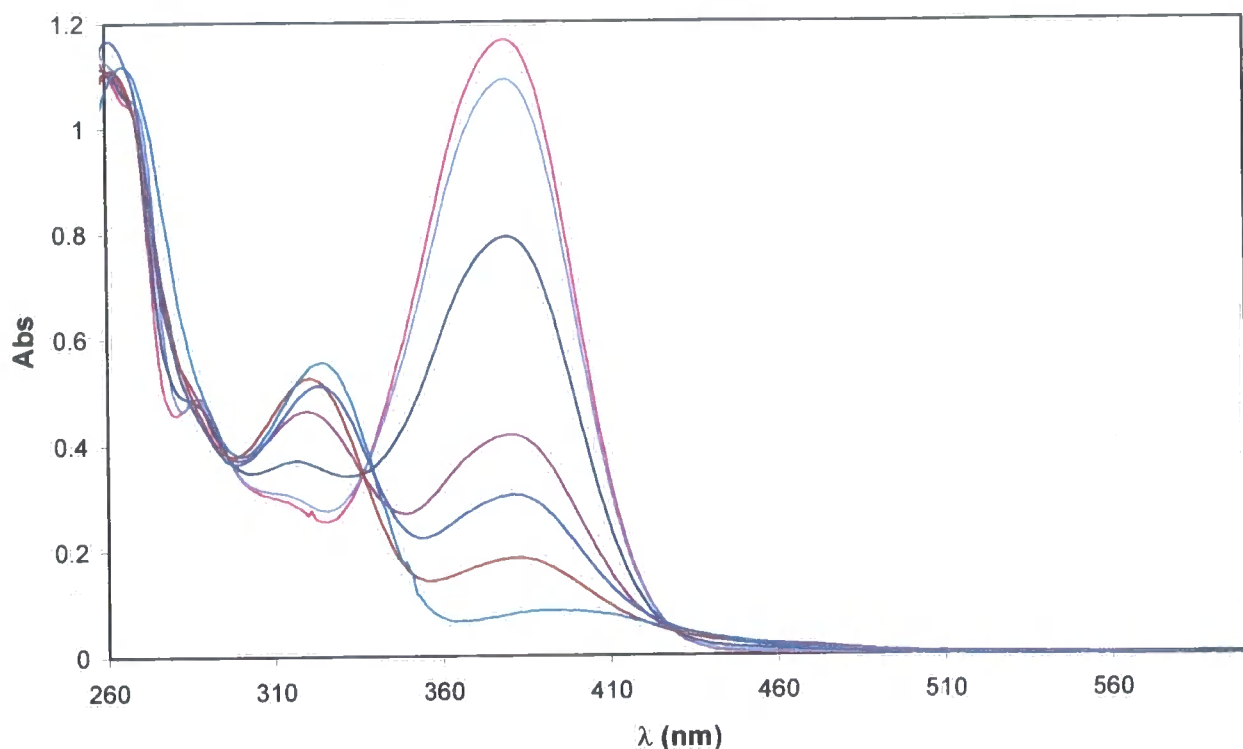
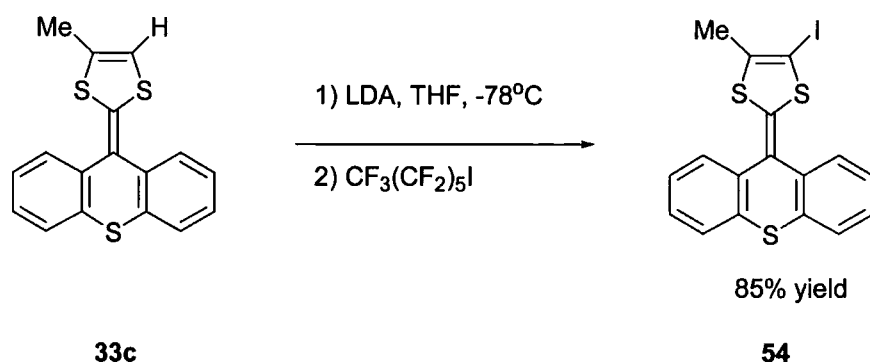


Figure 16. Spectroelectrochemistry: oxidation of **33a**.

5) Organometallic coupling reactions

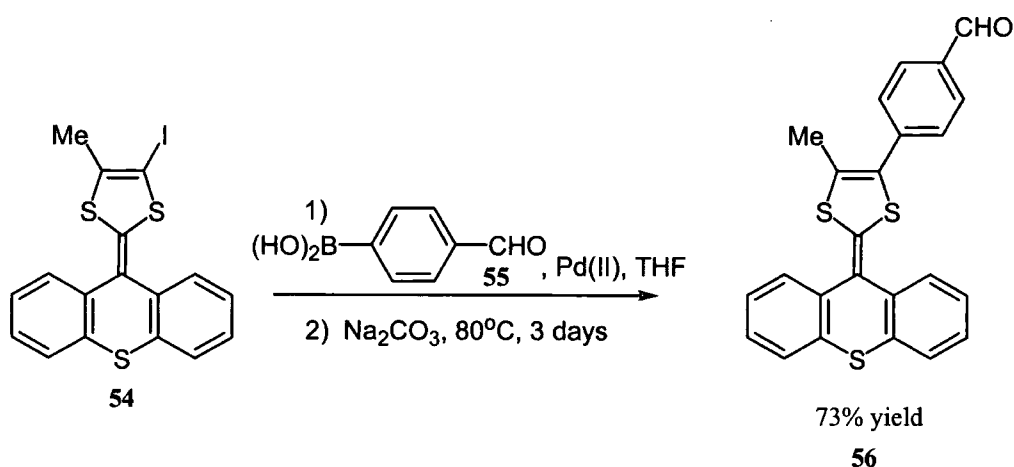
During the past two decades, enormous advances have been made in the area of transition-metal-mediated reactions in organic synthesis, e.g. Suzuki-Miyaura and Sonogashira coupling reactions ^[27-31]. Conjugated acetylenic compounds are especially valuable intermediates in organic synthesis for natural products, pharmaceuticals, and organic molecular materials such as molecular wires and molecular architectures on the nanometer scale. These compounds have frequently been synthesised by use of cross-coupling or self-coupling reactions to sp C atoms. The cross-couplings are reactions of alkynylmetal reagents with unsaturated organic halides, and of alkynyl halides with alkynyl-or arylmetal reagents ^[27, 28]. Organic iodides are known to be more reactive than the corresponding bromides or chlorides in these reactions.

In order to explore the scope for these types of reactions involving the 9-(1,3-dithiol-2-ylidene)thioxanthene system, we first targeted the iodo analogue **54**, by analogy with previous work in our laboratory on the synthesis of halogenated TTF derivatives ^[32]. Deprotonation of **33c** using LDA in THF at -78°C, followed by *in situ* trapping of the lithiated species with perfluorohexyl iodide gave the iodo derivative **54**, as a shelf-stable solid in a very good yield (85%) (Scheme 9). This stability of **54** is noteworthy as many iodo-TTF derivatives are known to decompose slowly by loss of iodine under ambient conditions ^[33].



Scheme 9.

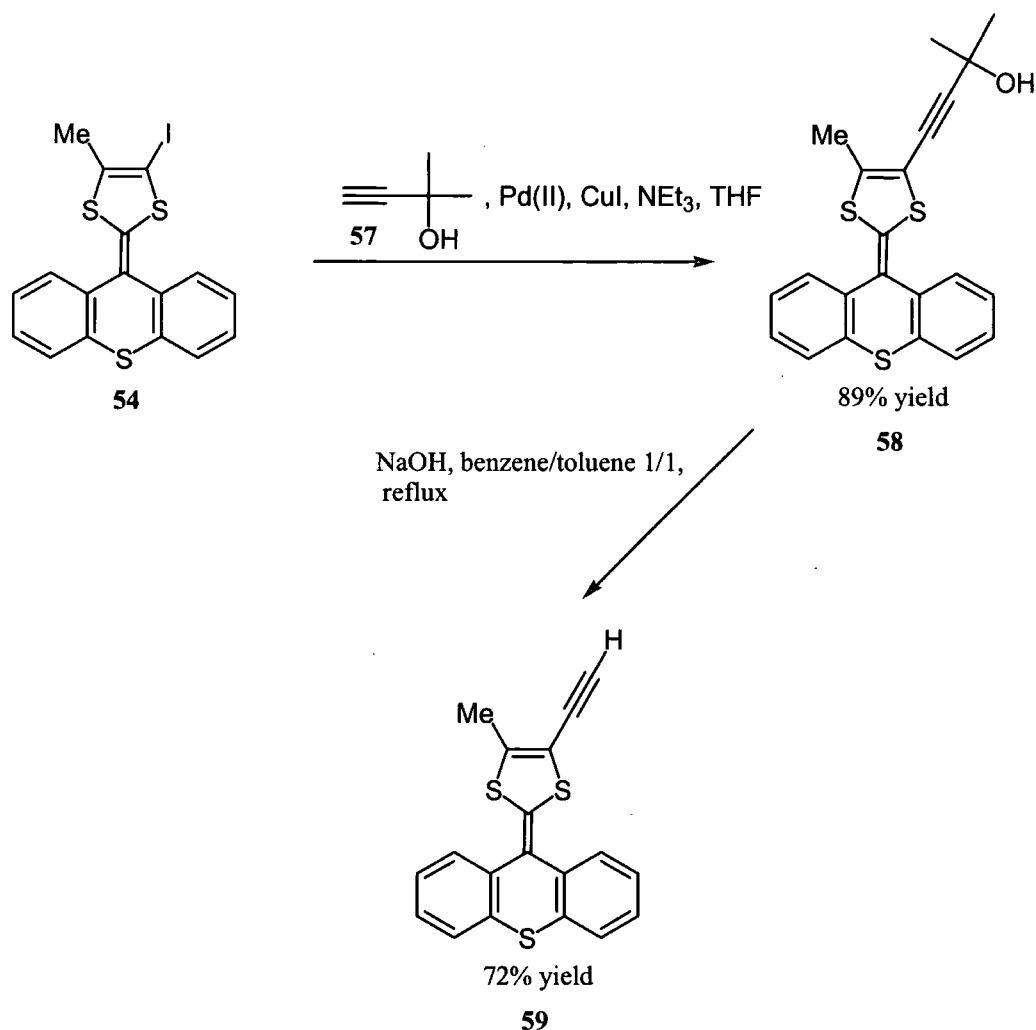
Following the success of this reaction, we were then able to explore cross-coupling reactions. Initially we examined the Suzuki coupling of **54** with a boronic acid. For this reaction we chose 4-formylbenzene boronic acid **55** with a view to utilising its aldehyde functionality in further synthetic steps. Reaction of **54** with **55** in the presence of dichloro-bis-(triphenylphosphino)palladium as catalyst and a solution of aqueous sodium carbonate as base in THF, with heating for three days, gave product **56** in 73% yield (Scheme 10).



Scheme 10.

We next turned to a Sonogashira cross-coupling^[27, 28], i.e. the coupling of the iodo derivative **54** with an alkyne. For this purpose, we chose alkyne **57** because there is experience with this reagent in our laboratory and it is known that the terminal polar hydroxy group assists in the purification of the cross-coupled product^[34]. The reaction of **54** with **57** in presence of dichloro-bis-(triphenylphosphino)palladium as catalyst, copper iodide and triethylamine in THF gave compound **58** (89 % yield) .

Deprotection of compound **58** using sodium hydroxide in a mixture of benzene/toluene 1:1 (v/v) as solvent, gave compound **59** (72% yield) (Scheme 11).

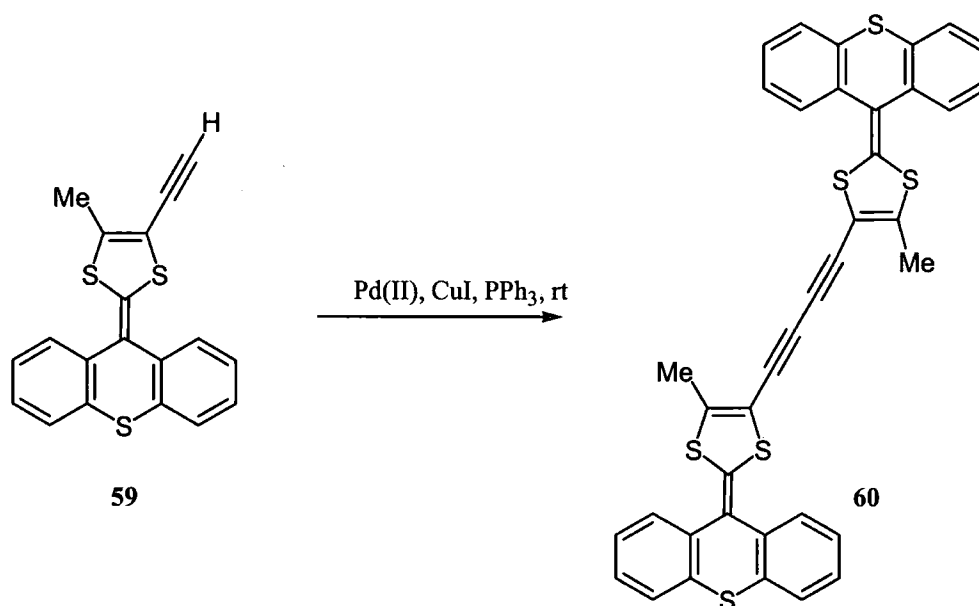


Scheme 11.

These reactions to yield **56** and **58** convincingly established that metal-catalysed cross-couplings of reagent **54** can occur in high yield, which is in contrast to many iodo-TTF derivatives, which tend to give low yielding reactions, and/or complex product mixtures, under these conditions^[35]. We were particularly interested in compound **59** as a potential precursor to its self-coupled dimer, with a view to studying its electrochemistry. Would we observe a single, four-electron oxidation process, or two different waves of two electrons each?

Thus we synthesised the dimer **60** from **59**, by a self-coupling reaction^[36], using a mixture of triethylamine/acetonitrile 2.5:1.5 (v/v) as solvent in presence of dichloro-bis-

(triphenylphosphino)palladium as catalyst, copper iodide and triphenylphosphine (Scheme 12). The yield of the reaction was very low (6%), these conditions do not work, the reaction needs an oxidising reagent to allow the palladium catalyst to be regenerated.



Scheme 12.

Studies on the cyclic voltammetry of **60** were complicated by its insolubility, which restricted the choice of solvents that could be used. We found that hot *o*-dichlorobenzene dissolved the dimer; unfortunately the conductivity in this solvent is quite low, and the only parameter, which we could vary, was the scan rate. Changing the scan rate between 10 and 1000 mV s⁻¹ did not alter the CV. We also encountered a problem of aggregation of the oxidised species on the working electrode, which we managed to overcome by the addition of acetonitrile. Thus, after much experimentation, the electrochemistry of **60** was studied in a mixture of acetonitrile/*o*-dichlorobenzene, containing tetrabutylammonium hexafluorophosphate as electrolyte (0.05 M), at 20 °C, with Ag/AgCl as reference electrode, scan rate 100 mV/s (Figure 15).

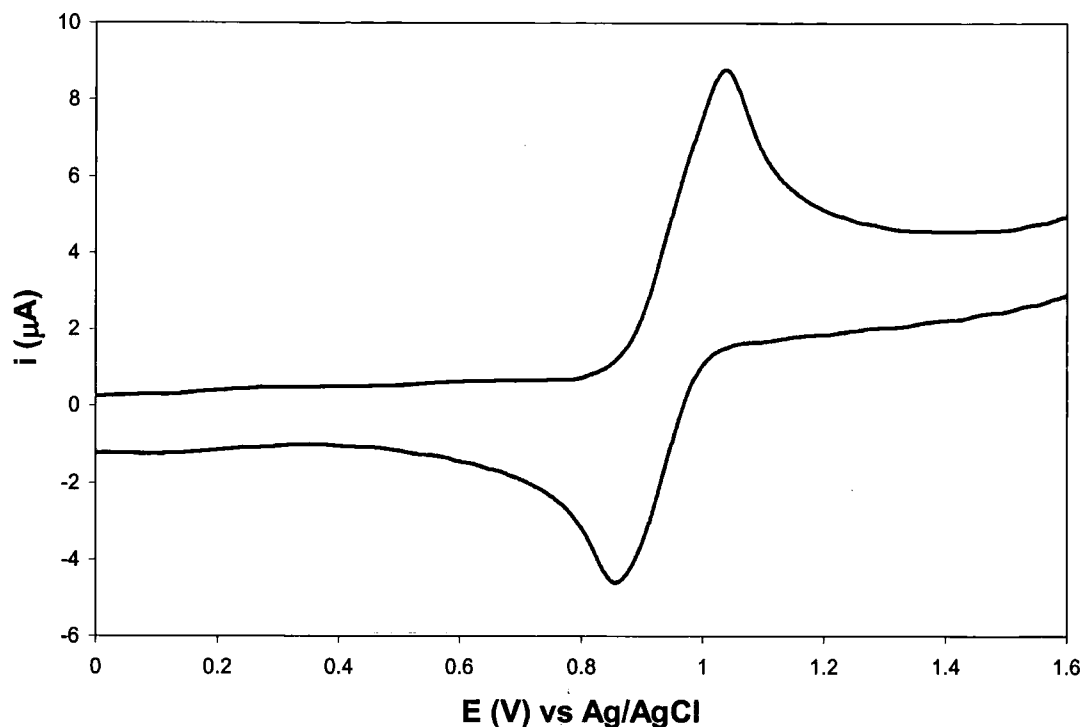
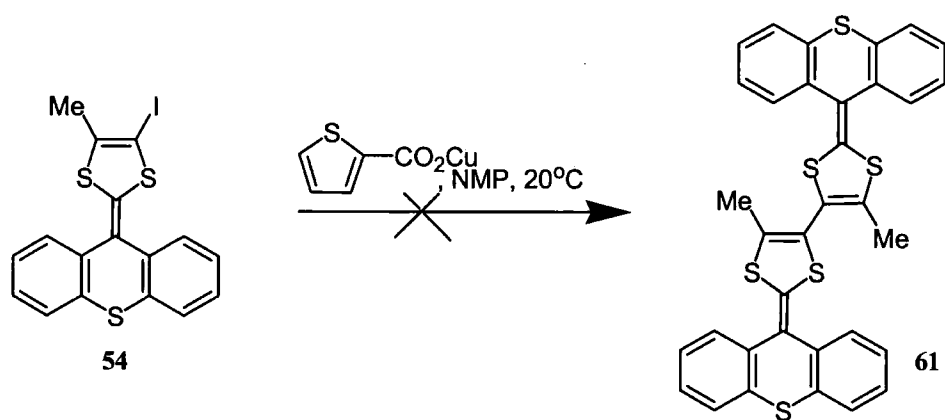


Figure 15. Cyclic voltammetry of **60** in MeCN/*o*-dichlorobenzene.

A clear oxidation wave is observed for **60** at $E^{\text{ox}} + 1.04$ V (with the coupled $E^{\text{red}} + 0.85$ V) which is consistent with a four-electron process arising from both donor units of the dimer being oxidised independently to the dication species and then reduced back to the neutral state without any observable intermediate species. The process is chemically reversible, in that recycling through this wave several times did not change the CV response.

We also attempted to synthesise the dimer **61** from the iodo derivative **54**, but without success. Heating **54** with copper powder in DMF ^[32], or with a solution of copper(I) thiophene-2- carboxylate in 1-methylpyrrolidin-2-one ^[32] (Scheme 13) resulted in no reaction (tlc evidence) and only starting material **54** was recovered. This unreactivity could be due to steric hindrance preventing the coupling from occurring.



Scheme 13.

CONCLUSIONS

We have synthesised a range of derivatives of the π -electron donor system 9-(1,3-dithiol-2-ylidene)thioxanthene **33** and from solution electrochemical studies we have established that this system undergoes a single, two-electron oxidation process, which is quasi-reversible. As for previous anthracene-TTFs, the X-ray crystal structure of the neutral molecule **33a** shows the thioxanthene part adopts a saddle-shape with a slight folding of the dithiole ring. Unfortunately, we could not obtain any crystals of dication salts suitable for X-ray analysis to study the change of conformation upon oxidation. Theoretical calculations performed in Professor Orti's group support these structural and electrochemical data, and show that the cation radical keeps this folded shape, whereas the dication comprises a planar thioxanthenium unit with an orthogonal ditholium cation. We succeeded in synthesising derivatives bearing covalently attached acceptor units, e.g. **43** and **44**, which showed intramolecular, charge transfer bands in the UV/Vis absorption spectra. Sulfoxide and sulfone derivatives, **51** and **52**, respectively, gave observable radical cation species.

Also, using the shelf-stable iodo derivative **54**, we demonstrated clean cross-coupling reactions under Suzuki-Miyaura and Sonogashira conditions in high yield, which is in contrast to many iodo-TTF derivatives. Further elaboration of the 9-(1,3-dithiol-2-ylidene)thioxanthene system to provide derivatives with extended π -conjugation is described in the next Chapter.

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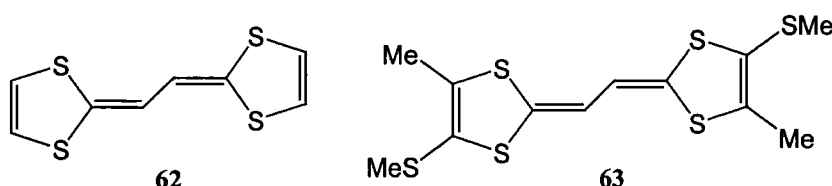
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CHAPTER THREE

CONJUGATED SYSTEM OF 9-(1,3-DITHIOL-2-YLIDENE) THIOXANTHENE DERIVATIVES

The next stage of this research was to explore the synthesis and properties of analogues of **33**, which possess an extended π -electron conjugation pathway. It is known that the insertion of vinylogous conjugation between the dithiole rings of TTF, e.g. structures **62** and **63** ^[1-3], decreases the oxidation potential of the system, compared to TTF, and favours the formation of dication salts for some systems, rather than radical cation salts.

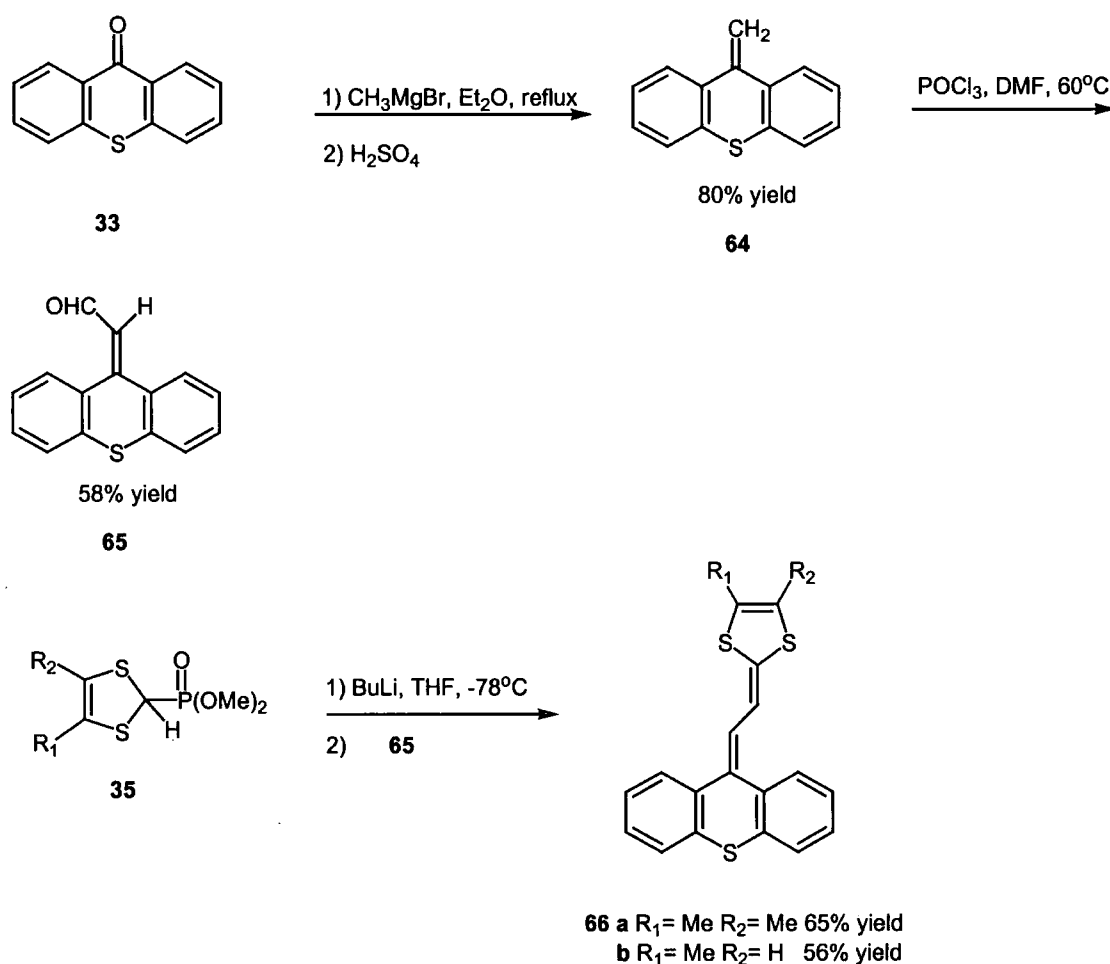


1) Synthesis

To obtain new extended systems, we first chose to prepare the methylene thioxanthene derivative **64**, which we identified as a precursor to the key building block **65** containing an aldehyde functionality suitable for Horner-Wadsworth-Emmons olefination, as described in Chapter 2. Compound **64** was prepared in 71% yield, as described in the literature by a Grignard reaction of methyl magnesium bromide, on thioxanthen-9-one **33** followed by the addition of sulphuric acid (Scheme 1).

The reaction of **64** with phosphorus oxychloride in DMF, and then neutralisation of this solution with sodium hydroxide, following precedents for related systems ^[4], cleanly gave compound **65** as a yellow solid in 58% yield. Key initial data to support structure **65** were the presence of the aldehydic proton and carbon atoms at δ 9.77 and δ 193.29 in the ^1H and ^{13}C NMR spectra, respectively.

Following the procedures described previously in Chapter 2, the phosphonate esters **35** were deprotonated with one equivalent of lithium diisopropylamide (LDA) in dry THF at -78°C , and the resulting anion was reacted with **65** to give the expected products **66**, which were isolated by column chromatography followed by recrystallisation, in moderate yields (Scheme 1).



Scheme 1. Synthesis of Horner-Wadsworth-Emmons derivatives **66a,b**.

Recrystallisation of the dimethyl derivative **66a** was achieved in ethyl acetate to form red crystals, which were analysed by X-ray diffraction (Figure 1).

In molecule **66a**, the dithiolebutadiene moiety, i.e. the atoms S(2), S(3), C(14), C(15), C(16), C(17), C(18), C(19) and C(20) with their hydrogens, are disordered between two orientations with occupancies 88.4(1)% (unprimed) and 11.6(1)% (primed). These orientations differ by configuration around the C(9)=C(14) bond and can be (roughly) described as related by the mirror plane of the thioxanthene moiety. Only the major position is shown in Figure 1 and discussed below. The thioxanthene folding is slightly less than in **52**, the benzene rings *A* and *B* forming an interplanar angle of 143.0°. The S(1) and C(9) atoms are essentially coplanar with ring *A* but displaced out of the plane of ring *B* by 0.06 and 0.10 Å, respectively. The dithiole ring is folded along the S(2)...S(3) vector by 4.7°. The butadiene chain is slightly twisted around the C(14)–C(15) bond, the planar moieties C(9)C(10)C(13)C(14) and C(15)C(16)S(2)S(3) forming a dihedral angle of 11.1°.

The oxidation of the S(1) atom does not affect the lengths of the S(1)–C bond [average 1.762(2) Å in **66a**], as well as C–C bonds in the thioxanthene moiety.

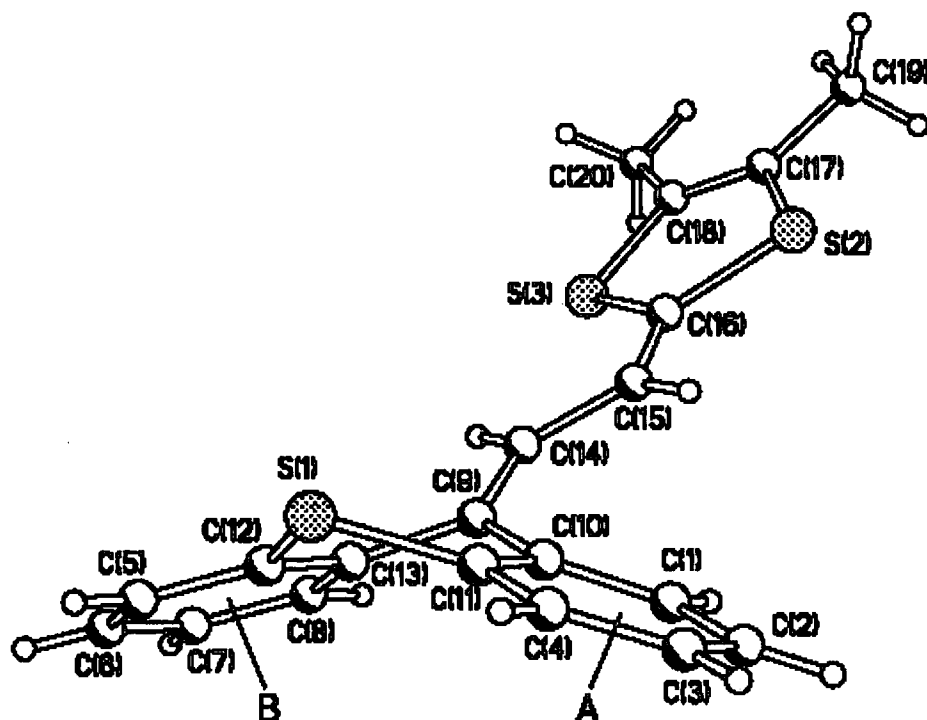
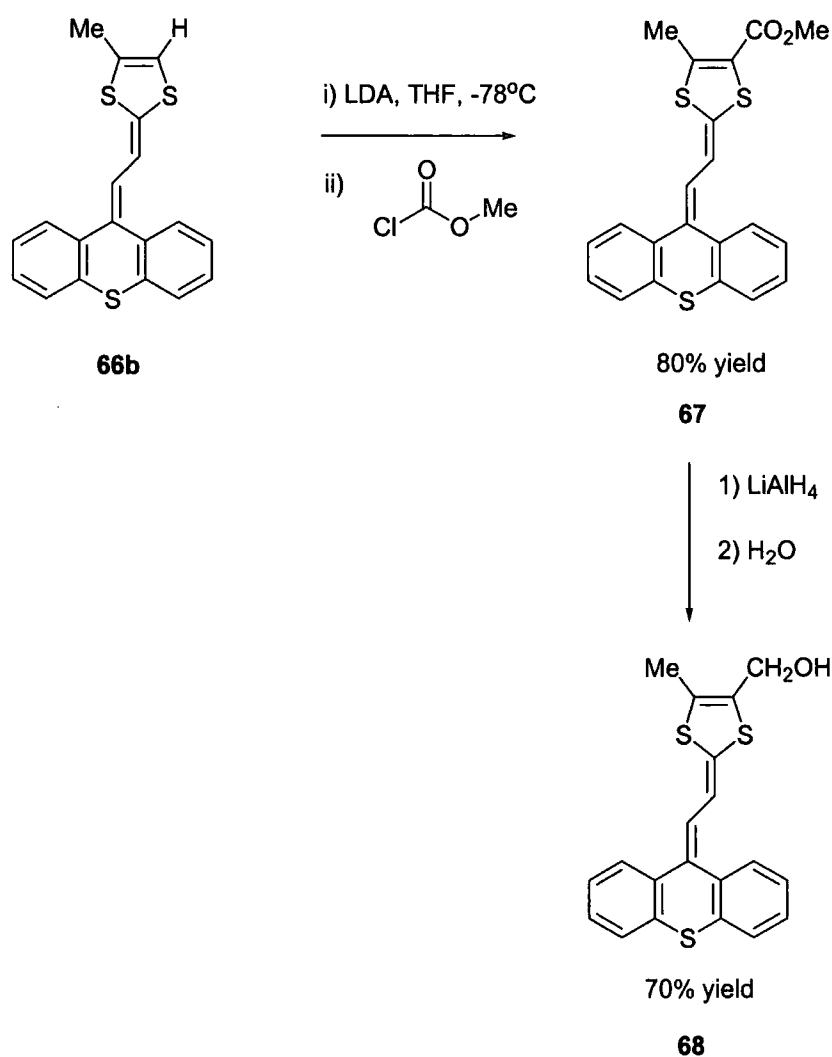


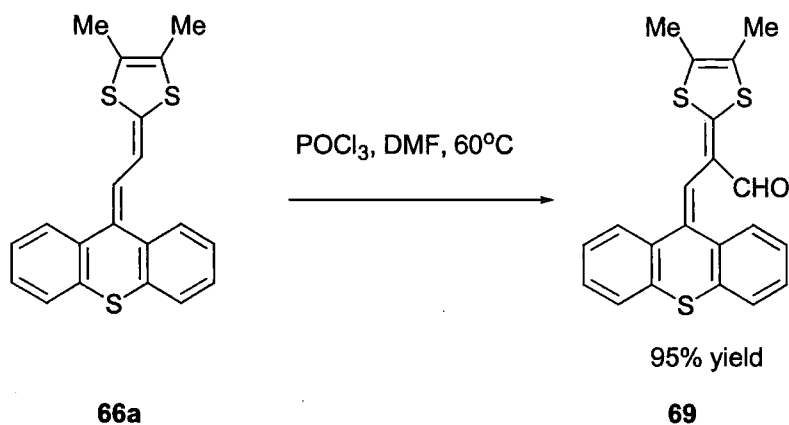
Figure 1. Molecular structure **66a** (minor component of the disorder is omitted).

The same reactions as described for system **33** have been carried out in order to increase the functionality in the molecule. Thus we used the mono-methyl analogue **66b**, which upon deprotonation with LDA in dry THF at -78°C , followed by *in situ* trapping of the lithiated species with methyl chloroformate gave the methyl ester derivative **67** (80% yield) which was reduced with lithium aluminium hydride to the hydroxymethyl derivative **68** (70% yield) (Scheme 2).



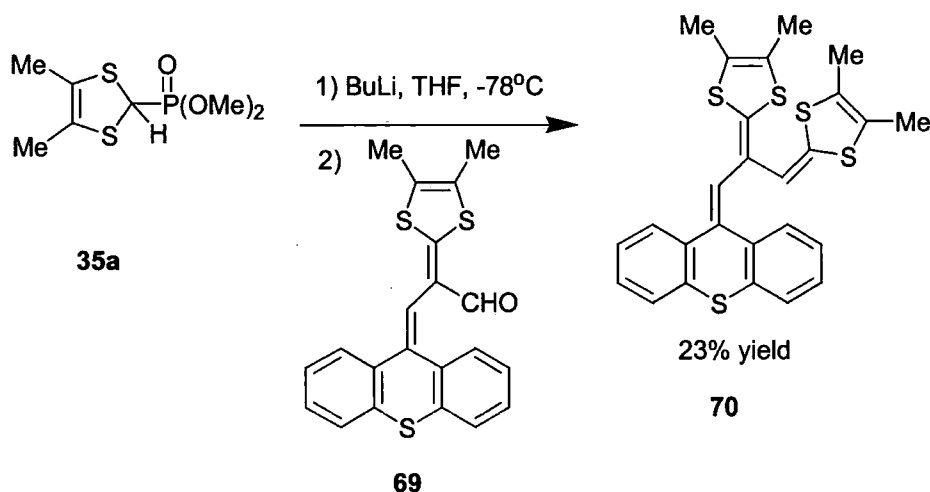
Scheme 2. Esterification followed by reduction of **66b**.

By analogy with the preparation of **65**, we obtained **69** in 95% yield from compound **66a** (Scheme 3). This compound is very interesting because we can use the aldehyde group to extend the conjugation and the functionalisation of **69** further, and thereby modify the redox behaviour of the molecule.



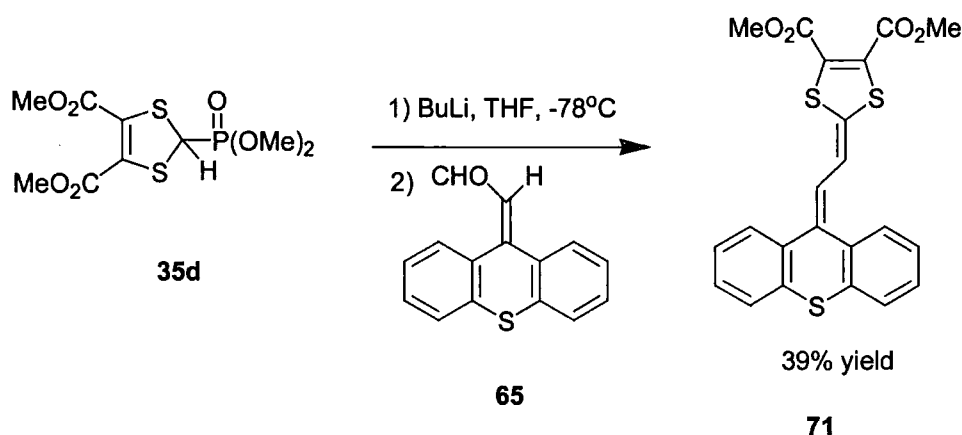
Scheme 3. Synthesis of **69** via a Vilsmeier reaction.

Thus, following the same literature route as for compound **66**, by using reagent **35a** we obtained the Horner-Wadsworth-Emmons reaction product **70** in 23% yield (Scheme 4).



Scheme 4. Synthesis of **70** via a Horner-Wadsworth-Emmons reaction.

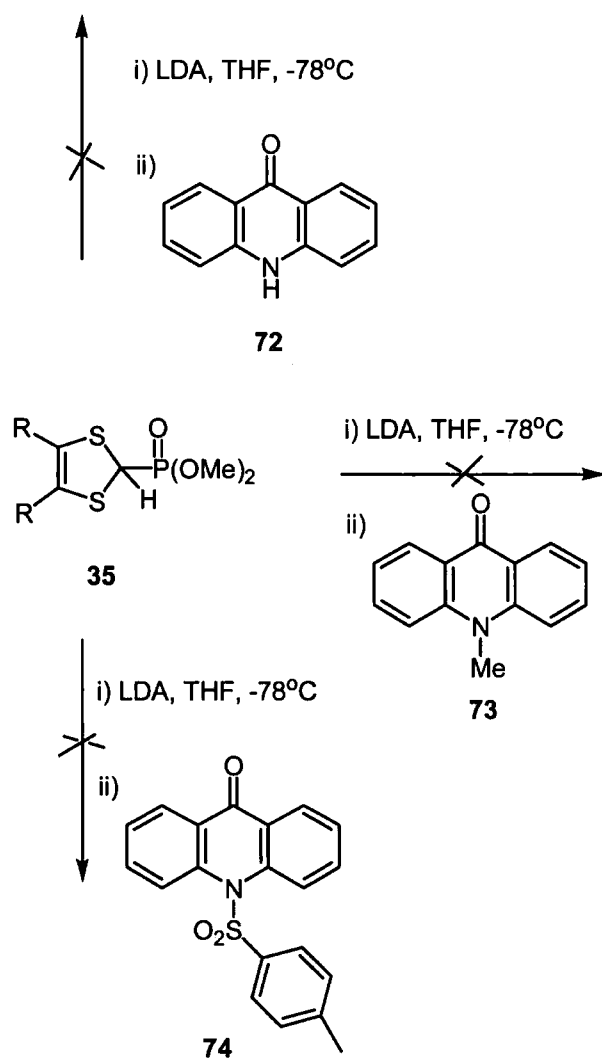
We also succeeded in obtaining the bis-methyl-ester derivative **71**, in 39% yield starting from the readily-available bis-ester phosphonate reagent **35d** ^[5], which undergoes a Horner-Wadsworth-Emmons reaction following the same conditions as previously ^[6], (Scheme 5). Unfortunately, the attempted reduction of **71** using lithium aluminium hydride as used for **37** did not give the corresponding bis-hydroxymethyl derivative: compound **71** was not recovered under the reaction conditions.



Scheme 5. Synthesis of **71** via a Horner-Wadsworth-Emmons reaction.

We also attempted to modify the properties of this family of compounds by preparing acridone analogues. Thus, we initially chose to react the parent acridone **72**, instead of the thioxanthene-9-one **34**, with reagent **35**. Unfortunately, no reaction occurred and compound **72** was recovered unchanged. To eliminate the possibility that base was deprotonating at NH, we repeated the reaction using methylacridone **73**, and the toluene sulfonyl acridone **74** ^[7] for which the N-substituent is electron-withdrawing and should therefore, increase the reactivity of the carbonyl group, but without any success: again, no reaction was observed (Scheme 6). Therefore, the attempted preparation of acridone analogues was abandoned. However, Ishikawa *et al.* managed to synthesise the phosphonate salt derivative from acridone and methyl acridone and then, by reaction with different ketones, to obtain the expected Horner-Wadsworth-Emmons products ^[8].

We attempted to repeat this procedure but without success. Therefore, acridone derivatives were not explored further.



Scheme 6.

2) Electrochemical and spectroscopic studies

The electrochemistry of the compounds listed in Table 1 has been studied by cyclic voltammetry in both THF and DCM, containing tetrabutylammonium hexafluorophosphate as electrolyte (0.1M), at 20°C, with Ag/AgCl as reference electrode, and 100 mV/s scan rate. Their UV/vis spectroscopic data in chloroform are included (Table 1).

Compound	E_{pa}^{ox}/V (THF)	E_{pc}^{red}/V (THF)	E_{pa}^{ox}/V (DCM)	E_{pc}^{red}/V (DCM)	λ/nm ($\epsilon/dm^3 mol^{-1}$ cm^{-1}) (CH_2Cl)
66b	1.09	-	0.95	-	391 (2.23×10^3)
67	0.84	-	0.75	0.70	406 (3.40×10^3)
68	0.69	0.46	0.63/ 0.81	0.46/ 0.67	417 (47.53×10^3)
69	0.87	-	0.86	0.71	429 (5.97×10^3)
70	0.56	0.37	0.36/ 0.68	0.22/ 0.52	389 (21.11×10^3) / 409 (20.65×10^3)

Table 1. Cyclic voltammetric data and UV/vis spectroscopic data for **66b**, **67**, **68**, **69**, **70**.

^a E_{pa}^{ox} is the oxidation peak potential on the first anodic scan; E_{pc}^{red} is the coupled reduction peak potential on the cathodic scan.

The comparison of the cyclic voltammograms in both solvents is very interesting. For instance, compound **66b** shows a single oxidation wave at E^{ox} 1.09 V, which is completely irreversible in both THF and DCM (Figure 3) and presumed to be a two-electron process, as was later confirmed by epr data (see below).

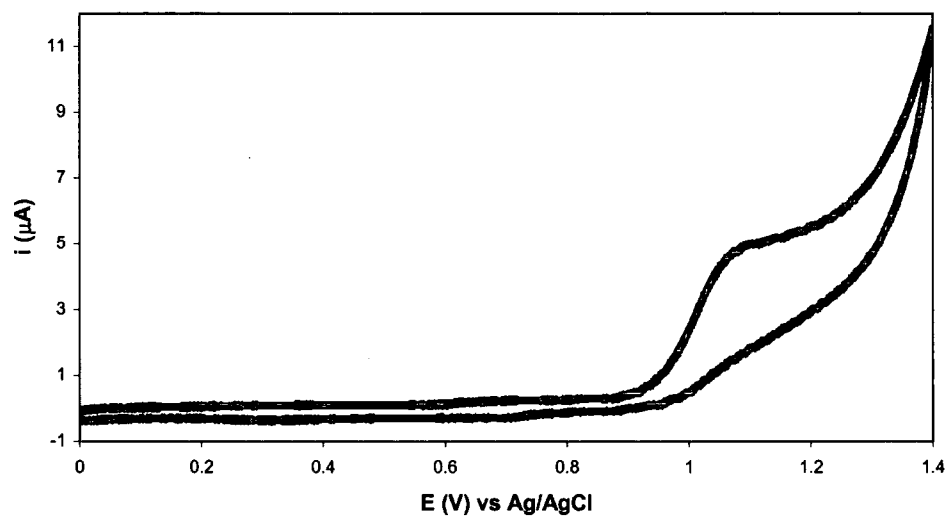


Figure 3. Cyclic voltammetry of **66b** in THF.

For compound **67**, the cyclic voltammetry also shows a single irreversible oxidation wave at E^{ox} 0.84 V in THF, whereas in DCM we can observe a fully reversible process at E^{ox} 0.75 V (Figure 4), which presumably involved two electrons, as was later confirmed by epr data (see below).

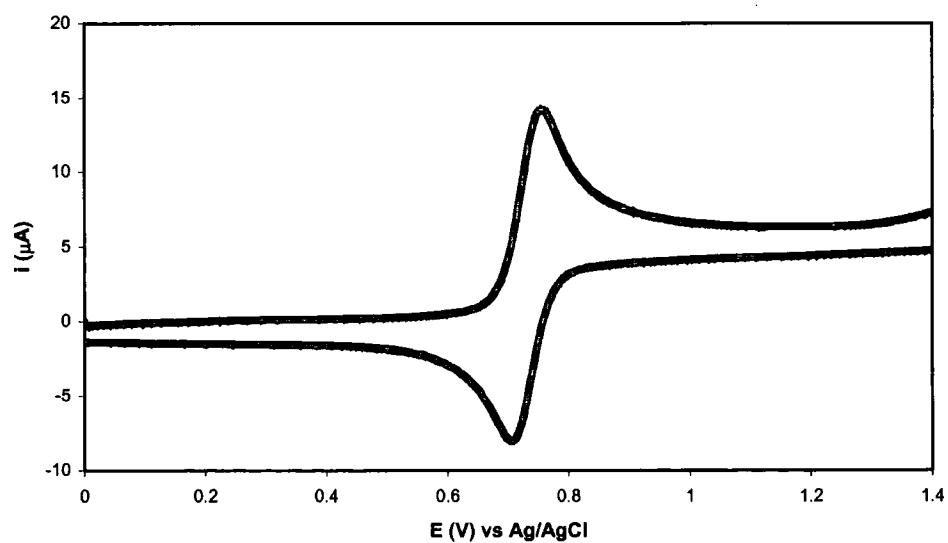


Figure 4. Cyclic voltammetry of **67** in DCM.

The same happened with compound **68**, where the difference is even more emphasised. Indeed, in THF we have seen the same behaviour as for compound **66b** and **67**, whereas in DCM we distinguished two, single-electron oxidation waves, E^{ox} 0.63 and 0.81 V, which are quasi-reversible (Figure 5). These waves are assigned to the sequential formation of the radical cation and dication species.

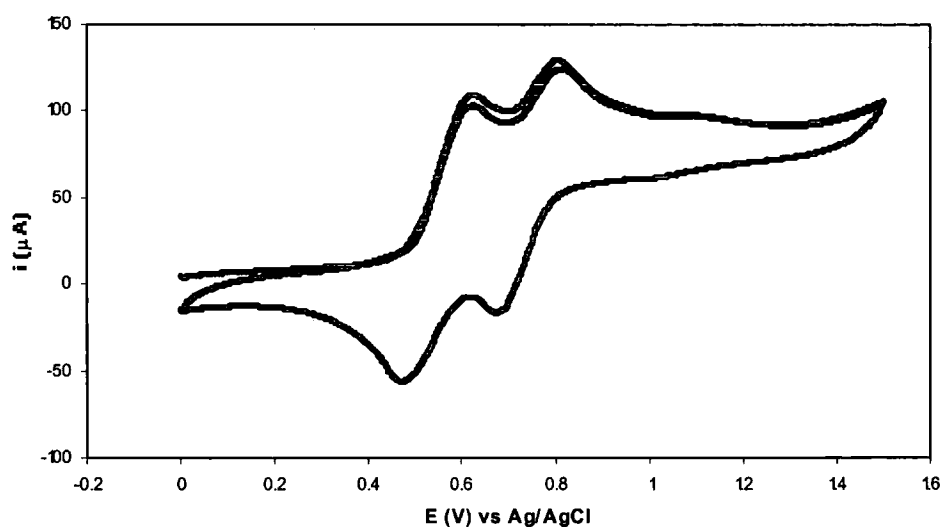


Figure 5. Cyclic voltammetry of **68** in DCM.

The same behaviour has been observed for compound **69**, which also shows a single, two-electron wave, irreversible in THF, but quasi-reversible process in DCM at E^{ox} 0.86 V (Figure 6).

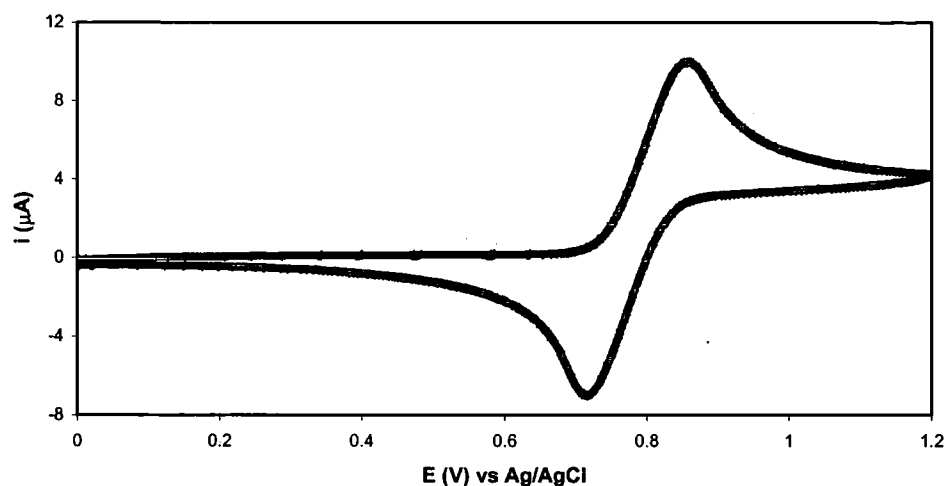


Figure 6. Cyclic voltammetry of **69** in DCM.

Finally, we observed similar behaviour for compound **70** as for compound **68**. Indeed in THF the cyclic voltammetry showed a single, irreversible, oxidation wave at E^{ox} 0.56 V, whereas in DCM we observed clear two, reversible one electron oxidation waves at E^{ox} 0.36 and 0.68 V (Figure 7). For compounds **68** and **70** intramolecular interactions along the conjugated backbone of the molecule can explain the sequential formation of the radical cation first, followed by the dication.

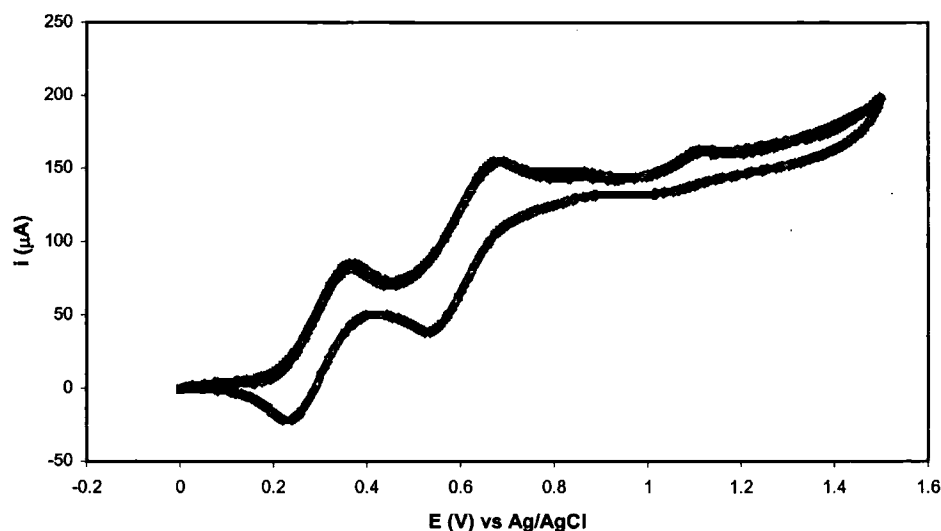


Figure 7. Cyclic voltammetry of **70** in DCM.

We attribute these marked solvent effects to different rates of diffusion of the species in THF and in DCM. Throughout all these experiments, we realised that the choice of solvent and experimental conditions is very important and can lead to significant changes in solution redox behaviour. Indeed, as we have seen above, the solvent plays a key role, depending on the solubility, the diffusion of the species, but also the electrolyte (to improve the conductivity of the solution) and the scan rate, which affect formation of oxidised species. It is a combination of all these factors, which leads to obtaining clean and reproducible cyclic voltammetric behaviour.

An overall trend is that increasing the conjugation has slightly lowered the oxidation potential, but not significantly so. However, the electrochemical behaviour observed for compounds **66b**, **67** and **68** were completely unexpected compared to those of the first series of derivatives **33a**, **36**, **37** and known TTF vinylogues ^[1-3] and are difficult to explain.

We have also recorded the UV/vis absorption spectra of compounds **66b**, **67**, **68**, **69**, and **70** in chloroform solution. A common feature of the spectra is the absorption band in the region λ_{max} 391 nm and 429 nm, which is consistent with their yellowish colour (Figure 8). A small red shift (ca. 20 nm) of the absorbance of these compounds is observed compared to the first series synthesised (compounds **33a-c**, **36**, **37**) and this can be readily ascribed to the additional π -conjugation.

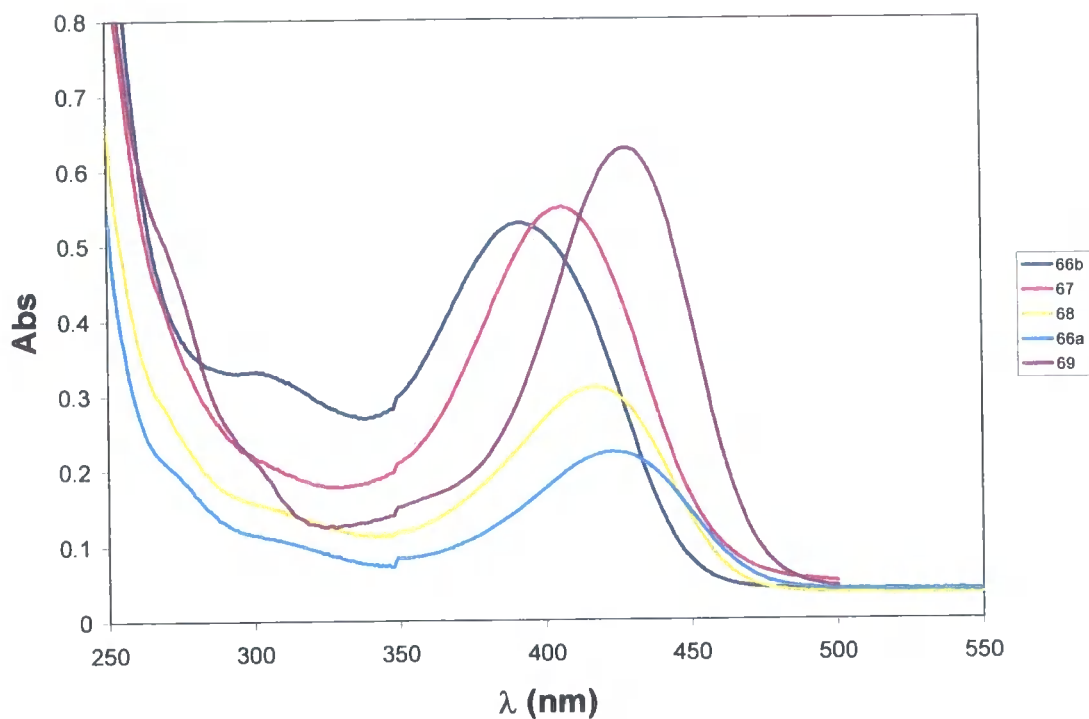


Figure 8. UV/vis absorption spectra of **66b**, **67**, **68**, **66a**, **69**.

By analogy with system **33**, we expected the ester derivative **67** to have the shortest wavelength absorption in this series. However, this is not the case: it is observed for its precursor **66b**, (**66b** λ_{max} 391 nm; **67** λ_{max} 406 nm). This series follows a logical progression in spectroscopic absorption behaviour as seen for the TTF series in Chapter 2 ^[9]. Thus, compound **69** follows the expected behaviour by being the most red shifted (λ_{max} 429 nm), which can be explained by an extension of the conjugation due to the aldehyde function.

The UV/vis absorption spectrum of **70** shows two overlapping bands at λ_{max} 389 nm and 409 nm; this is probably due to interactions between the two dithiole rings. The presence of an additional red-shifted shoulder in the region 450-500 nm could arise from intramolecular charge transfer along the molecule (Figure 9).

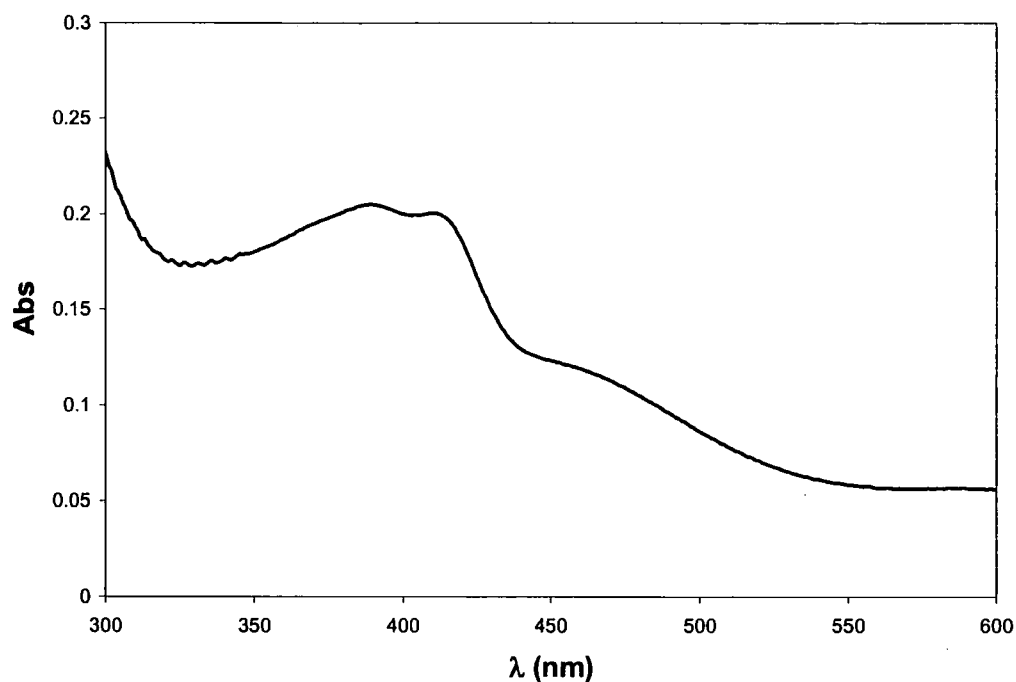


Figure 9. UV/vis absorption spectrum of **70** in CHCl_3 solution.

3) EPR studies and electrocrystallisation experiments

We studied the epr spectroscopic properties of compounds **66b**, **67** and **68** in order to compare with their cyclic voltammetric behaviour. For instance, as discussed above, the electrochemistry of **66b** was not clear, so we sought to clarify the oxidation process, which was occurring using simultaneous electrochemistry and epr (SEEPR) studies. So we oxidised **66b** progressively, with the aim of gaining information on whether oxidation occurs in one step to the dication or in two steps via a radical cation intermediate.

The epr spectra of **66b** was monitored by SEEPR in a solution of 0.2M Bu_4NPF_6 in DCM at $E = 0.85$ V.

The simulated spectrum (Figure 10) is asymmetric revealing the presence of more than one radical. In fact we can distinguish two radical species, a first one unidentified, characterised as below: g-factor: 2.0070; line width: 0.4 Gauss. The second species,

which is shown in the simulation spectrum, coupling with one nucleus of spin $\frac{1}{2}$, a proton, was characterised by:

hyperfine coupling constant = 6.5 Gauss; g-factor = 2.0053; line width = 4 Gauss.

We can confidently assign this second species to the radical cation of compound **66b** because of the similarity of these data with known TTF derivatives ^[10].

Upon increasing the potential to $E = 1$ V the epr signal disappeared consistent with oxidation to the dication species. These data have helped us to understand that the oxidation of **66b** occurs in two steps at very similar potentials, by first forming the radical cation, and then the dication which we could not distinguish by cyclic voltammetry.

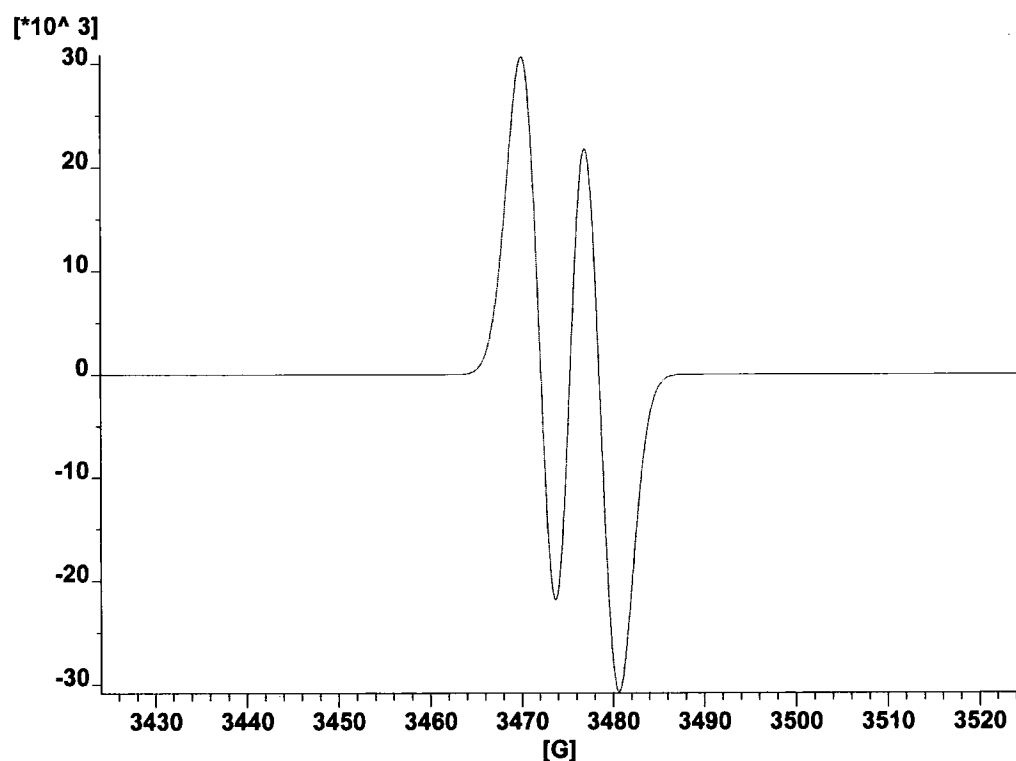


Figure 10. Simulated epr spectrum of **66b**.

The comparable study was undertaken for compound **67** but no epr signal was detected; this allows us to conclude that the oxidation process of this molecule occurs in one, two-electron step, to afford the dication, which is epr silent.

For compound **68**, when the SEEPR experiments were recorded in a solution of 0.2 M Bu₄NPF₆ in DCM at $E = 0.85$ V (Figure 11), we observed two different radicals, one of which was not stable and disappeared within 10 min of its generation, so we characterised only the more stable one. This radical is coupling with one nucleus of spin $\frac{1}{2}$, a proton, and is characterised by: hyperfine coupling constant = 6.75 Gauss; g-factor = 2.0065; line width = 2 Gauss.

Thus we can assign this signal to **68** because its characterisation is similar to the ones detected for previous derivatives. Again after increasing the potential we observed the disappearance of the signal due to the formation of the dication. Thus the epr and the cyclic voltammetry data are in agreement.

The radical cation of **68** has been generated chemically, using trifluoroacetic acid as the oxidising reagent in a solution of DCM at 20°C. Under these conditions we also observed a weak epr signal corresponding to the formation of a radical with the same characterisation parameters as that generated electrochemically. The epr studies of the radical cation of **68** generated via chemical or electrochemical oxidation are in agreement.

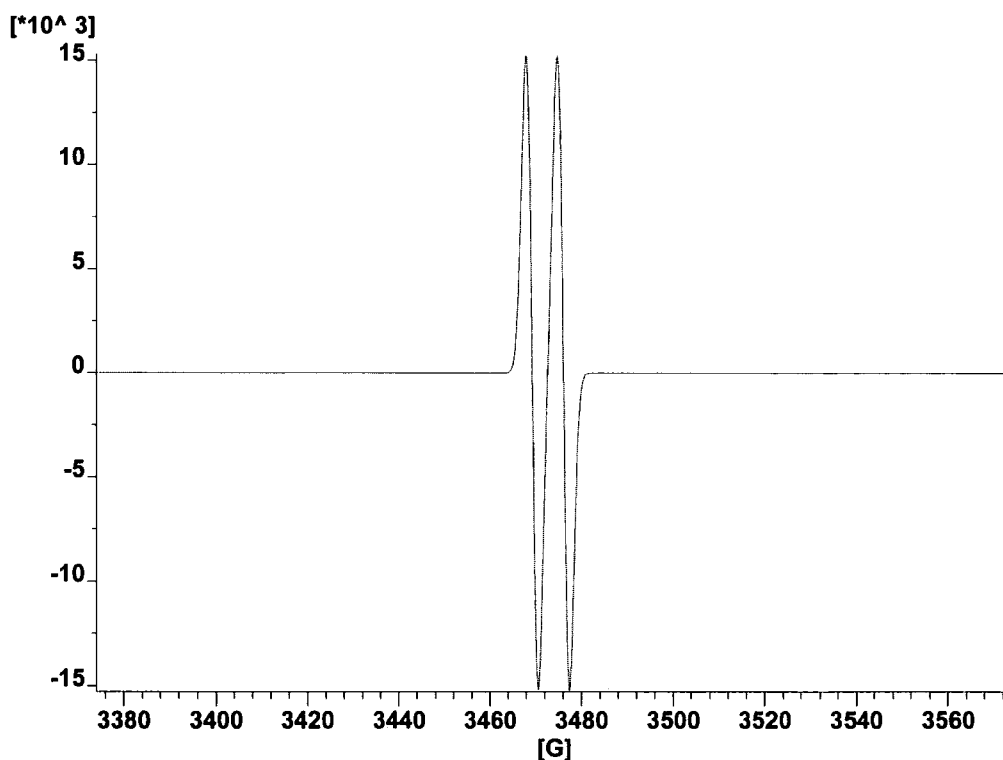


Figure 11. Simulated EPR spectrum of **68**.

The same studies have been realised for compound **70** to characterise its radical cation intermediate upon oxidation. The epr spectrum was obtained at $E = 0.4$ V in a solution of 0.2 M of Bu_4NPF_6 in DCM (Figure 12). The spectrum confirms the presence of a radical species, coupling with one nucleus of spin $\frac{1}{2}$, a proton, characterised as: hyperperfine coupling constant = 5.40 Gauss; g-factor = 2.0069; line width = 3.30 Gauss.

We can assign this signal to the radical cation of **70** because its characterisation is similar to the ones detected for previous derivatives.

The epr data were then obtained at $E = 0.7$ V where we could observe a decreasing signal until its complete disappearance, and then at $E = 1.15$ V there was still no signal. The epr study is in total agreement with the cyclic voltammetry.

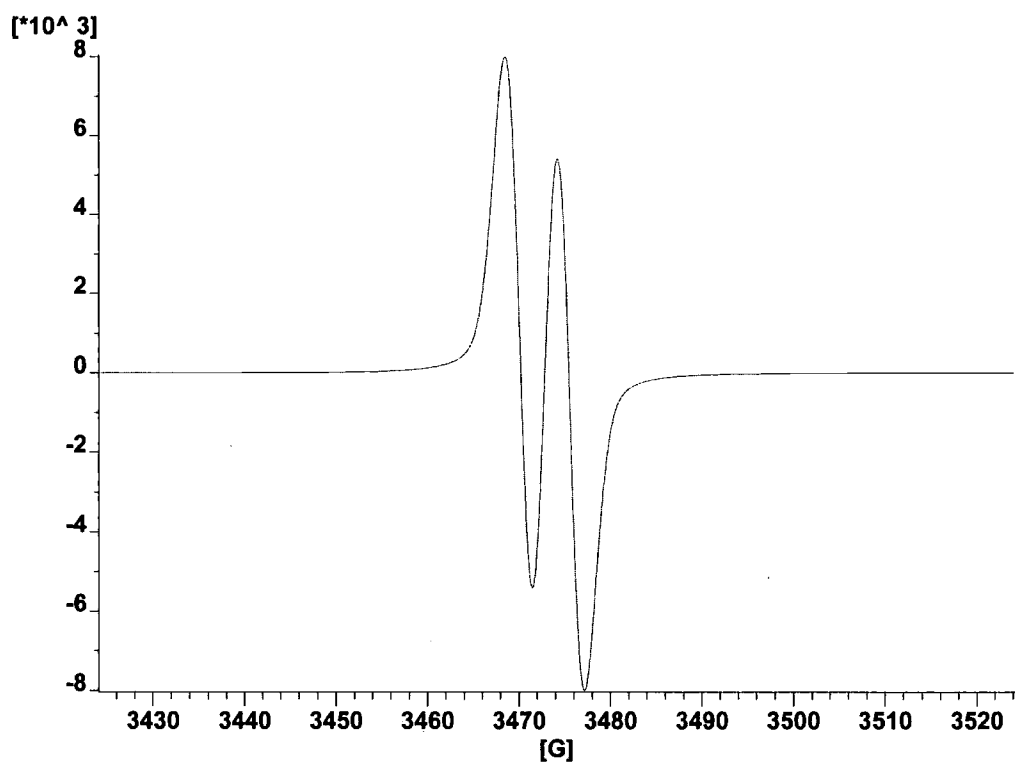


Figure 12. Simulated epr spectrum of **70**.

We also attempted to grow crystals of dication salt of **68** and **70**, electrochemically. All the attempts are summarised below (Table 1,2):

Solvent	Electrolyte	Fix potential	Current	Temperature	Electrode	Time	Result
chlorobenzene	Bu ₄ NPF ₆	30.4V	0.8μA	RT	Thick	6 days	Small crystals
chlorobenzene	Bu ₄ NClO ₄	30.4V	0.8μA	RT	Thick	8 days	Dication solution
chlorobenzene	Bu ₄ NAuI ₂	30.4V	0.8μA	RT	Thick	6 days	Small crystals
chlorobenzene	Bu ₄ NBr	17.7V	1μA	RT	Thick	12 days	No oxidation
chlorobenzene	TBA Pt (mnt) ₂	30.4V	0.7μA	RT	Thick	5 days	No oxidation
chlorobenzene	TBA Ni (mnt) ₂	30.4V	0.7μA	RT	Thick	5 days	No oxidation
chlorobenzene	TBA Au (mnt) ₂	30.4V	0.7μA	RT	Thick	5 days	No oxidation
THF	Bu ₄ NBr	17.7V	1μA	RT	Thick	12 days	No oxidation
THF	Bu ₄ NAuI ₂	17.7V	1μA	RT	Thick	12 days	Decomposition
THF	Bu ₄ NPF ₆	6V 13V	2μA 1μA	RT	Thick	7 days	No oxidation
THF	Bu ₄ NClO ₄	6V 13V	2μA 1μA	RT	Thick	7 days	No oxidation

Table 1. Electrocrystallisation performed on 68.

Solvent	Electrolyte	Current	Temperat	Electrode	Time	Result
chlorobenzene	Bu ₄ NPF ₆	0.7μA	RT	Thick	12 days	No oxidation
chlorobenzene	Bu ₄ NClO ₄	0.7μA	RT	Thick	12 days	Small crystals
chlorobenzene	Bu ₄ NAuI ₂	0.7μA	RT	Thick	12 days	No oxidation

Table 2. Electrocrystallisation of **70**.

We managed to collect small crystals of oxidised species from compound **68** and **70**, but unfortunately not suitable for X-ray crystal structure analysis. However, we analysed them by epr in the solid state, and both samples showed a signal revealing the presence of radicals in the crystals with the same characteristics as seen previously. We can therefore conclude that the crystals salts obtained by electrochemical oxidation are mixed valence.

CONCLUSION:

In this Chapter, we succeeded in synthesising a second series of novel extended derivatives of **33** based on the routes used previously. However, the electrochemical properties of these new systems were quite unexpected. Indeed, we expected a significant lowering of the oxidation potential, which was not observed.

However, the epr studies greatly assisted our understanding of the oxidation process involved in these derivatives. For some compounds intermediate radical cations were observed by epr and CV studies.

Finally it appeared that the extension of the π -system favoured the formation of crystalline salts of oxidised species, but further attempts at crystal growth are needed to obtain single crystals, which are suitable for X-ray analysis.

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CHAPTER FOUR

C₆₀ DERIVATIVES

1) Introduction

a) Description and properties

The spherical π -conjugated all carbon fullerene C₆₀ was discovered by Kroto, Smalley and Curl in 1985 [1]. Since the development of a facile method for the large-scale synthesis of fullerenes in high purity [2], the availability of these appealing molecules has allowed the exploration and development of their chemistry. Among the fullerenes, C₆₀ is the most attractive molecule due to its symmetrical geometry. The parent C₆₀ and its derivatives have been widely studied due to the remarkable range of organic material properties which they display (i.e. superconductivity, ferromagnetism, non-linear optical and photoinduced charge-transfer properties) [3] and also for their bio-medical properties (anti-viral activity) [4]. One of the physical characteristics of C₆₀ is its insolubility in polar solvents and its tendency to form aggregates under certain conditions [5]. It has been established by cyclic voltammetry that C₆₀ is a moderately good electron-acceptor able to accept up to six electrons in solution in a series of six sequential one-electron steps [6]. Spectroscopic studies on C₆₀ have shown that fullerenes strongly absorb in the ultra-violet region and moderately in the visible region. The absorbance at λ_{max} 430 nm is responsible for the purple colour of the solutions of C₆₀ [7].

Diads and polyads resulting from the covalent linkage of C₆₀ fullerene as the π -acceptor with various π -donors are very attractive compounds, prone to undergo a photoinduced electron transfer and they are established as very useful for the realisation of new artificial photosynthetic systems or photovoltaic cells [8, 9].

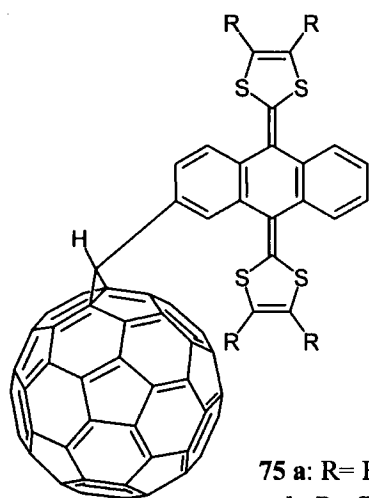
b) Preparation of C₆₀ adducts

The electrochemical behaviour of C₆₀, along with the possibility of linking a functional group to its carbon framework, through a great variety of cycloaddition reactions, without altering its electron-acceptor properties, has made C₆₀ a very interesting building block for novel molecular materials with remarkable electronic, magnetic and biological properties. Up to now, several electron-donor fragments have been attached to the C₆₀ cage, and in some cases, the final bichromophoric compounds show interesting intramolecular electronic interactions between the fullerene moiety and the addend. Three main reactions have been reported for the synthesis of these adducts [10].

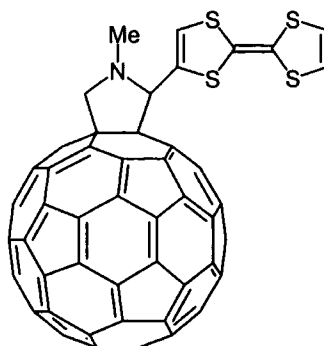
The Bingel reaction is a very common method and allows the donor to be attached directly to the C₆₀ unit (e.g. compound **75**) [11]. Another method, namely 1,3 dipolar cycloaddition of an azomethine ylide, consists of covalently linking C₆₀ through a flexible pyrrolidine bridge forming donor-acceptor diads (e.g. compounds **76**, **77**) [12].

Finally, these adducts can be synthesised by a [4+2] Diels-Alder cycloaddition, consisting of the linking of C₆₀ and a donor moiety by a rigid bridge such as a cyclohexene ring (e.g. compound **78**) [13]. This method has been adopted to promote electronic interactions in the diads; such interactions have never been reported for diads synthesised via a 1,3 dipolar cycloaddition, which is probably due to the large distance between the redox active centers and the relatively flexible bridge between them [10].

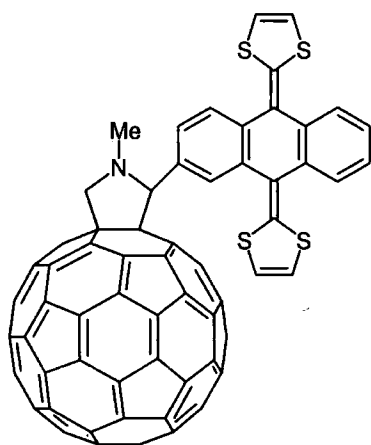
The combination of TTF and anthracene-TTF with C₆₀ (compounds **75-78**) has yielded some of the longest lifetimes for radical pairs (τ = ca. 100 μ s) ever reported for charge-recombination in intramolecular donor-acceptor systems that have comparable separation distances between the donor and acceptor moieties [14, 15]. This has been ascribed to the fact that the oxidised state of these donors is aromatic, which favours charge separation and decelerates charge recombination (loss of aromaticity) [13]. From this viewpoint we sought to attach C₆₀ to the 9-(1,3-dithiol-2-ylidene)thioxanthene electron donor framework.



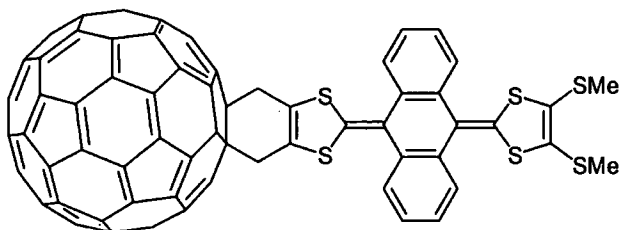
75 a: R= H
 b: R= SCH₃
 c: R= SCH₂CH₂S



76



77



78

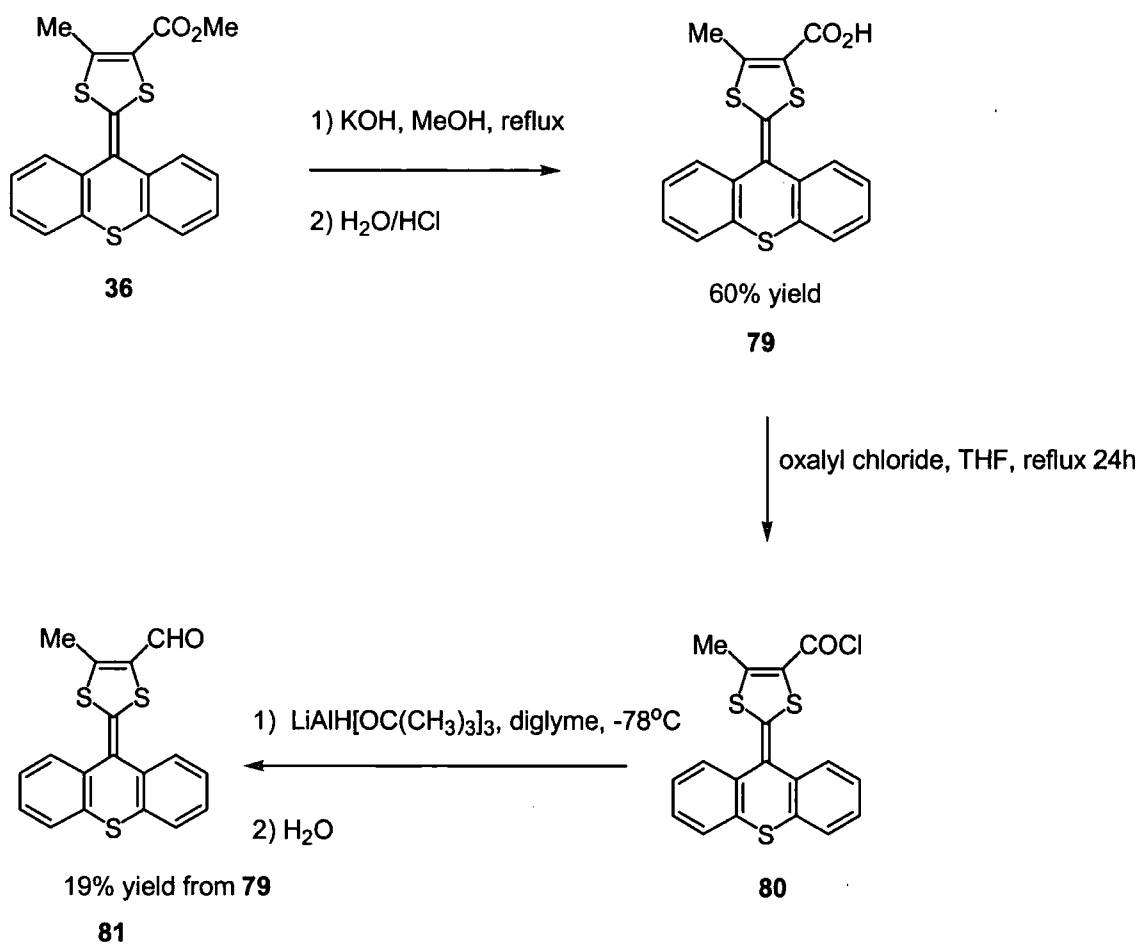
2) Synthesis of aldehyde derivatives of 9-(1,3-dithiol-2-ylidene)thioxanthene

In order to attach C₆₀ to system **33**, we chose to use the azomethine ylide dipolar cycloaddition route, which required the preparation of the aldehyde containing derivative. Several attempts were made to achieve this aim. The first route we explored consisted of deprotonation of the mono methyl derivative **33c**, using LDA at – 78°C in dry THF, followed by the addition of both DMF and *N*-methyl formanilide as the electrophile. However, no reaction took place, and we recovered the starting material **33c**.

We note that although this protocol is efficient with TTF (82% yield) ^[16, 17], and trimethyl-TTF (88% yield) ^[18], it is low-yielding with trimethyl-TTF-anthraquinone (13% yield) ^[19]. We then attempted to get aldehyde **81** by oxidation of the hydroxymethyl analogue **37** using two different methods. We used first a solution of selenium dioxide in dioxane ^[20], and secondly a solution of pyridinium chlorochromate in dry DCM. But unfortunately, in both cases compound **37** was destroyed, possibly because the oxidising reagents also reacted at sulfur atoms in the molecule.

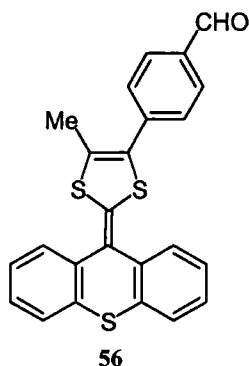
We also attempted a procedure using diisobutylaluminium hydride as reducing agent on the ester derivative **36**, but we recovered the starting material. Finally we were successful using a different multi-step procedure. Ester **36** was hydrolysed into the corresponding carboxylic acid **79** (60% yield) with a solution of potassium hydroxide (Scheme 1).

By reaction of **79** with oxalyl chloride in dry DCM, we generated the resultant acid chloride **80**, which had to be used immediately in the next step because of its instability. Reduction of **80** with lithium tri-*t*-butoxyaluminumhydride in diglyme ^[21] gave the desired compound **81** in 19% yield (Scheme 1).



Scheme 1.

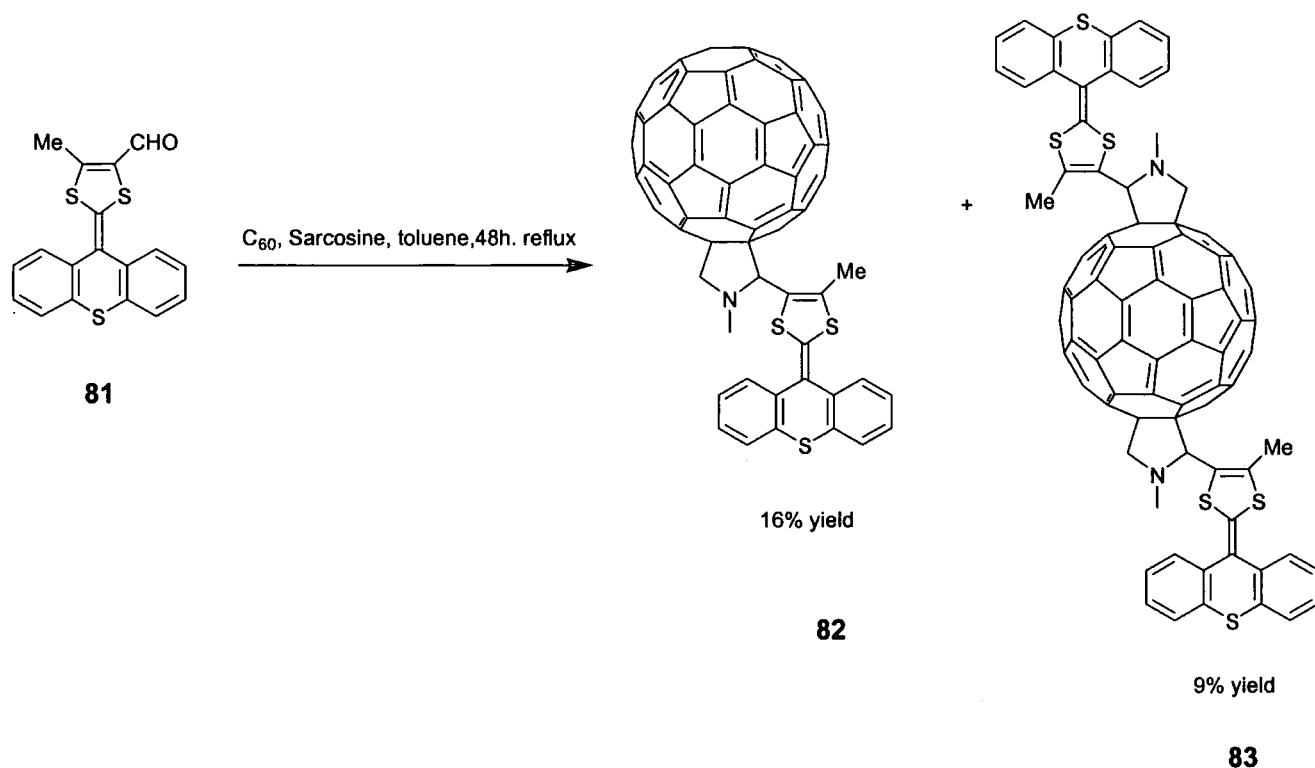
As described previously in Chapter 2, we managed to synthesise another aldehyde derivative through Suzuki cross-coupling reaction, namely compound **56**. So with these two aldehyde derivatives in hand we proceeded to the synthesis of donor-acceptor diads with C₆₀.



3) Synthesis of C₆₀ derivatives

In general, the synthesis of C₆₀-donor diads by this cycloaddition methodology is not difficult although purification of the product requires a lot of care; the yield of the reaction is in general quite low due to polyadditions. To achieve the attachment of C₆₀ to the aldehydes **81** and **56**, we followed Prato's procedure ^[22], which requires the use of a linker such as a pyrrolidine ring. For this purpose we added two equivalent of sarcosine to a mixture of C₆₀ and aldehyde in dry toluene and the solution was refluxed for 48 hours. The resultant products of both reactions have been purified by chromatography on silica gel using carbon disulfide as the eluent.

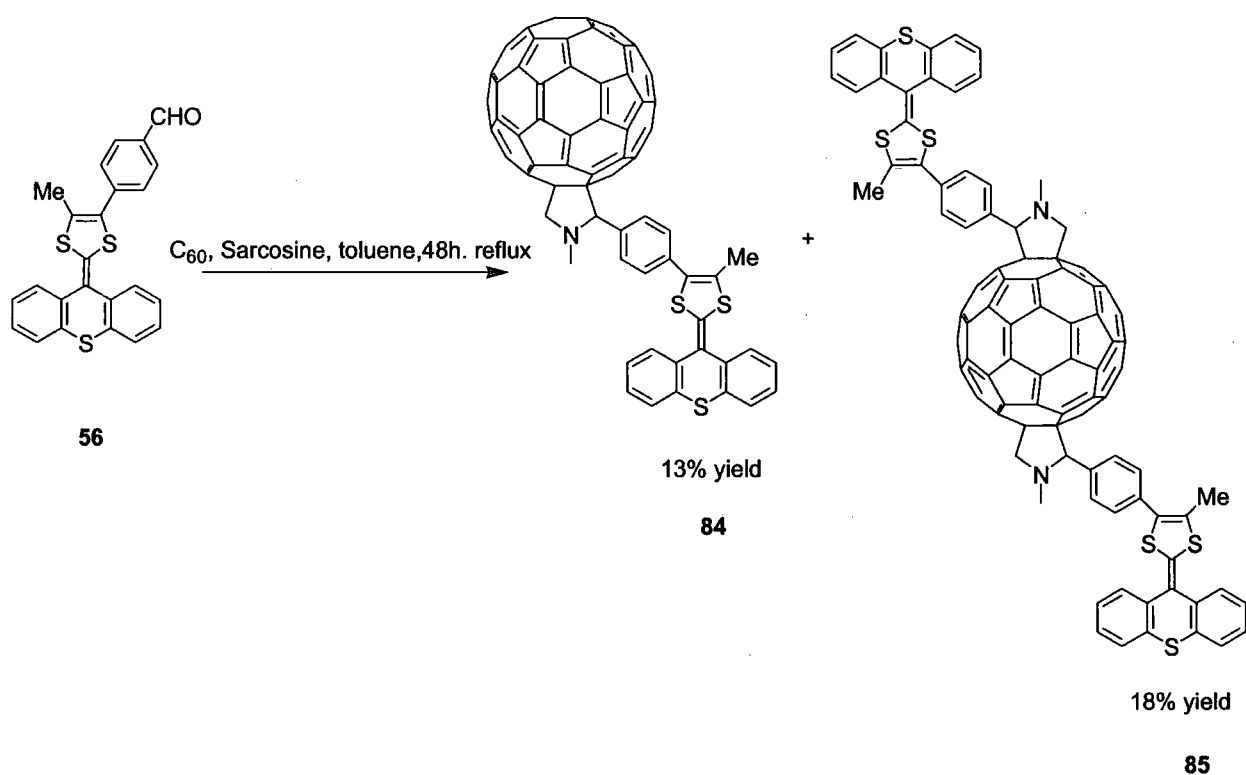
From compound **81**, we succeeded in isolating the mono-adduct **82** in 16% yield and the bis-adduct **83** in 9% yield (Scheme 2). As mentioned above, these low yields have literature precedents.



Scheme 2.

Concerning compound **56**, we isolate the mono-adduct **84** (13% yield) and the bis-adduct **85** (18% yield) (Scheme 3), and curiously we obtained the bis-adduct in the higher yield which is quite unusual; the mono addition is normally favoured compared to the bis addition. The bis-adducts **83** and **85** will be a mixture of different regioisomers.

We repeated the reaction with **56** and confirmed these yields. The most likely explanation is that there is some decomposition of the mono-adduct under the reaction conditions or during chromatographic purification, leading to the prevalence of the bis-adduct **85** as the isolated product. Evidence to support structures **82**, **83**, **84** and **85** came from ^1H NMR spectroscopy, UV/Vis absorption spectra and cyclic voltammetry. We were not able to obtain the parent ions in the MALDI-TOF mass spectra, which showed only fragments for compound **85** of the mono-adduct and for all the compounds the presence of C_{60} .



Scheme 3.



4) Electrochemical and spectroscopic studies

The electrochemical studies on all the adducts were difficult to perform because of their low solubility in a range of organic solvents. The most common solvents used for studies of this type of C₆₀ derivative are toluene, or ortho-dichlorobenzene; the compounds are soluble but the diffusion of the solutions is weak.

a) Compound 82:

We performed cyclic voltammetry experiments on the mono-adduct **82** in a mixture of acetonitrile/ortho-dichlorobenzene, containing tetrabutylammonium hexafluorophosphate as electrolyte (0.05 M), at 20°C, with Ag/AgCl as the reference electrode, and a scan rate of 100 mV/s (Figure 1).

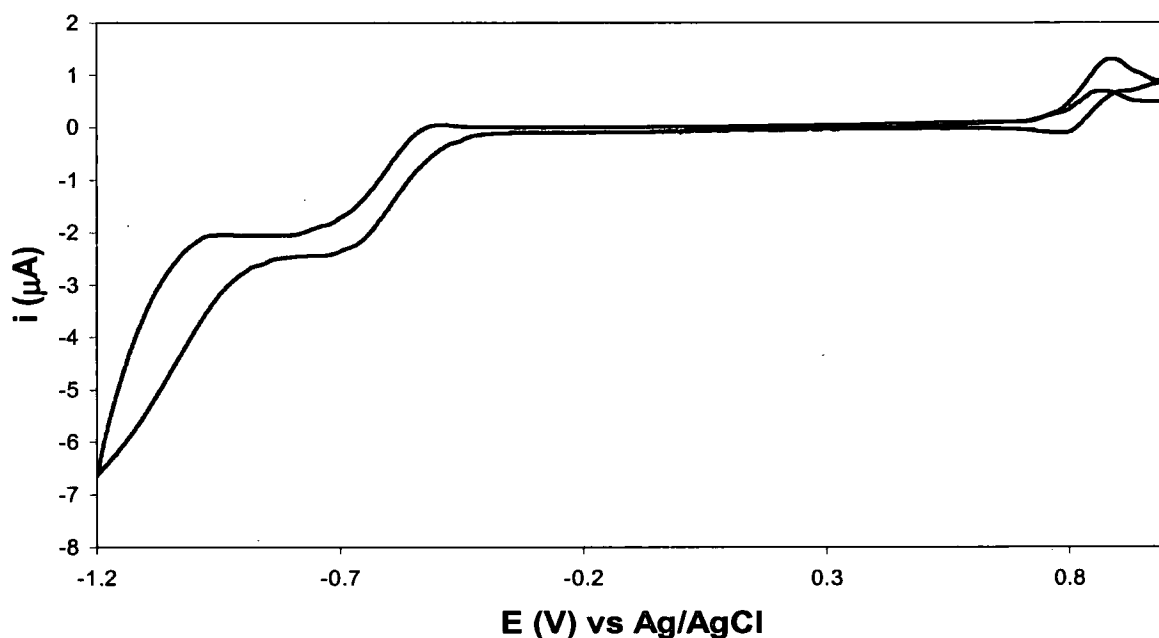


Figure 1. Cyclic voltammetry of **82** in MeCN/*o*-dichlorobenzene.

We clearly observed the quasi-reversible redox wave of the donor moiety at E^{ox} 0.89 V, presumably involving two electrons as for compound **33**, but unfortunately we could distinguish only one reduction wave for the C₆₀ part at E^{red} -0.50 V which is not reversible. After a second scan, we noticed the disappearance of the donor wave in the CV; this could arise from either the instability of compound **33** or aggregation of the compound around the working electrode due to poor diffusion of the species. Further experiments such as repeated scans and/or a change of the scan rate, and polishing of the electrode established that the cause was aggregation on the working electrode preventing detection of the donor oxidation wave.

Concerning the bis-adduct **83**, we studied the cyclic voltammetry in *ortho*-dichlorobenzene, containing tetrabutylammonium hexafluorophosphate as electrolyte (0.05 M), at 20°C, with Ag/AgCl as reference electrode, and a scan rate of 100 mV/s (Figure 2).

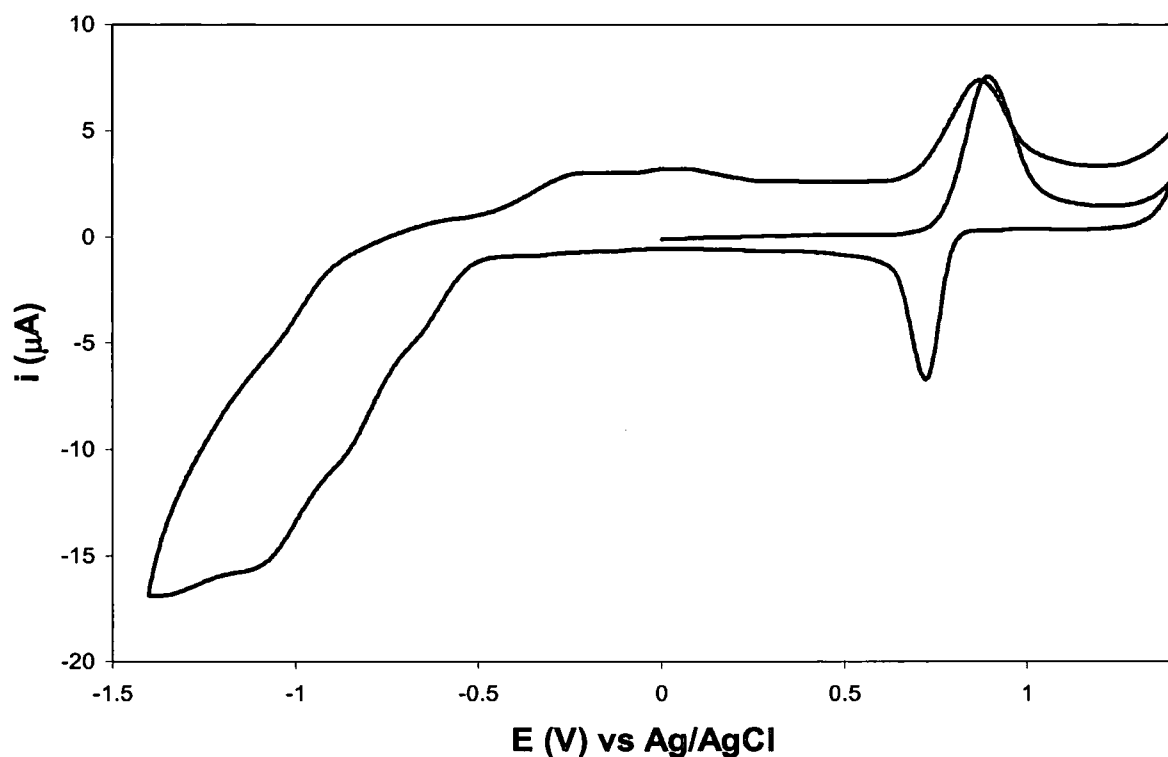


Figure 2. Cyclic voltammetry of **83** in *o*-dichlorobenzene.

As for the mono-adduct **82**, we observed the oxidation of the donor and the coupled reduction wave with a peak separation of 190 mV (E_{pa}^{ox} 0.90 V; E_{pc}^{ox} 0.71 V). We could just about observe three poorly resolved waves on the cathodic scan at negative potentials, which can be tentatively attributed to sequential reduction of the C₆₀ fragment. But we again encountered diffusion problem due to the solvent and the size of the molecule.

The UV/Vis absorption spectra of these species were more enlightening. Indeed, for compound **82** (Figure 3) we observed the characteristic absorbance band of the donor fragment at λ_{max} 381 nm, and the characteristic bands of C₆₀ at λ_{max} 314, 713 nm, and in particular the band at 436 nm is typical of mono-addition having occurred to C₆₀ [23].

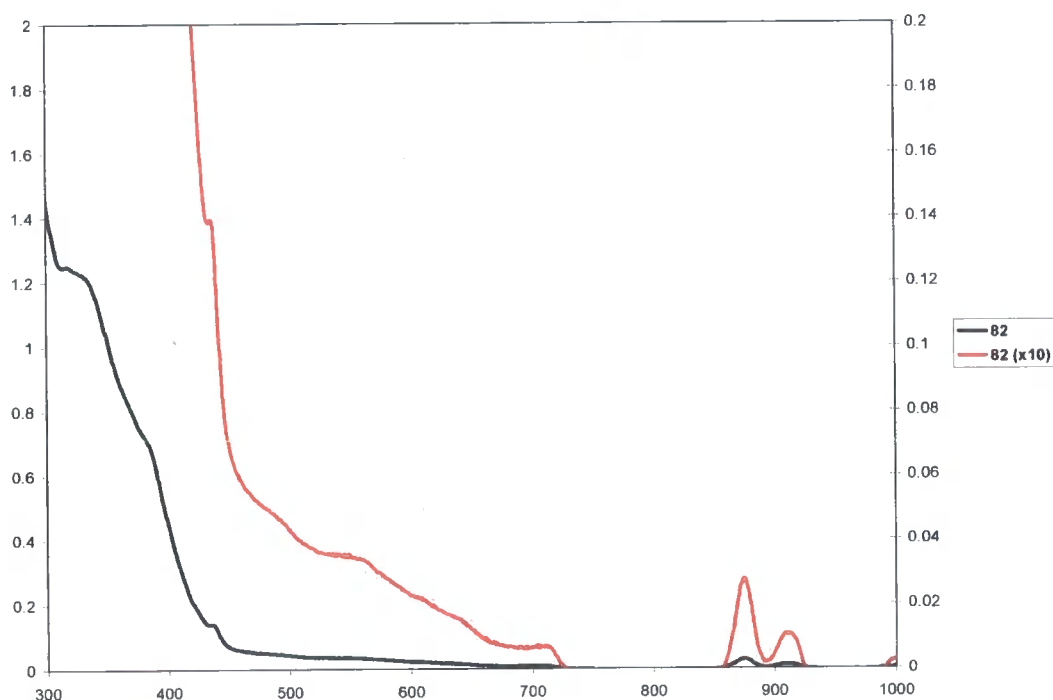


Figure 3. UV/vis absorption spectrum of **82**.

For the spectrum of the bis-adduct **83** (Figure 4), we observed similar absorption bands, albeit slightly blue shifted for the donor at 369 nm, but notably with the disappearance of the characteristic band of mono addition at 436 nm, thereby providing strong support for the assigned structure of the product. Two additional absorbance bands of low intensity are observed at λ_{max} 875 and 911 nm in the spectra of both **82** and **83**, which are very similar to those observed in other solid essentially neutral complexes formed by C_{60} and TTF derivatives^[24, 25]. These bands have been assigned to a very small degree of intermolecular charge transfer arising from short intermolecular C...S contacts between the donors and the C_{60} molecule. In summary, these bands indicate the existence of very weak inter- or intra-molecular interactions between the donor and acceptor moieties^[10].

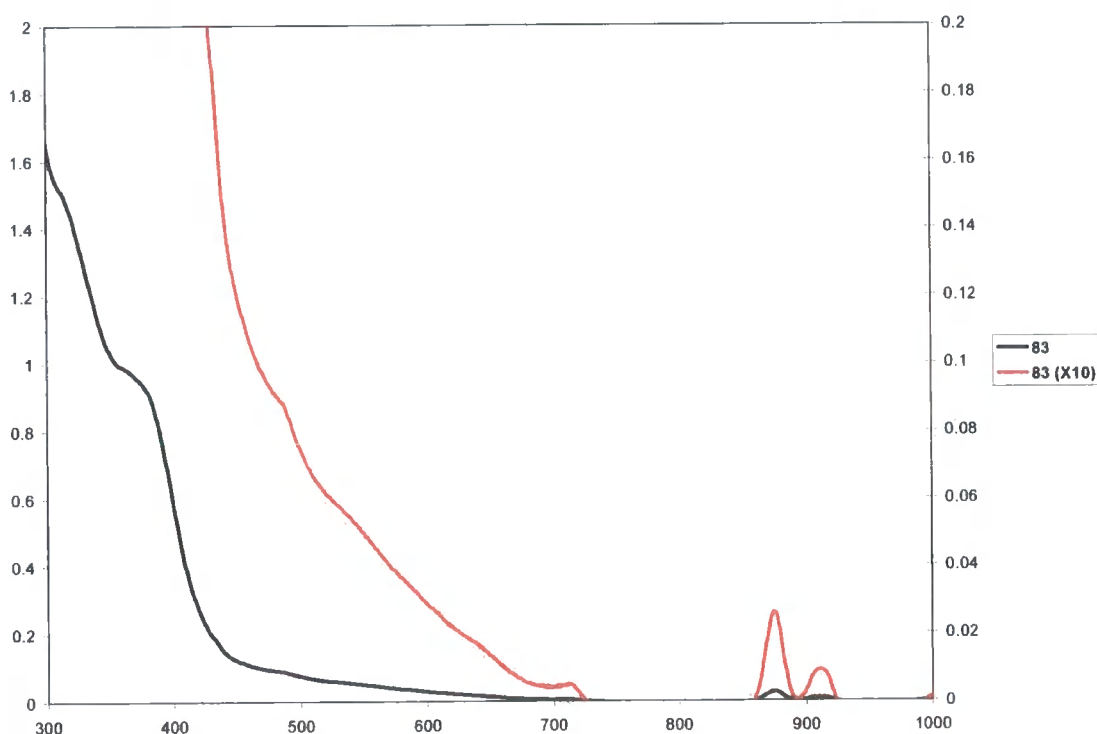


Figure 4. UV/vis absorption spectrum of **83**.

b) Compound 84:

We also performed comparable CV experiments on mono- and bis-adducts **84** and **85**. The CV of mono-adduct **84** in *ortho*-dichlorobenzene, containing tetrabutylammonium hexafluorophosphate as electrolyte (0.05 M), at 20°C, with Ag/AgCl as reference electrode, and a scan rate of 100 mV/s is shown in Figure 5.

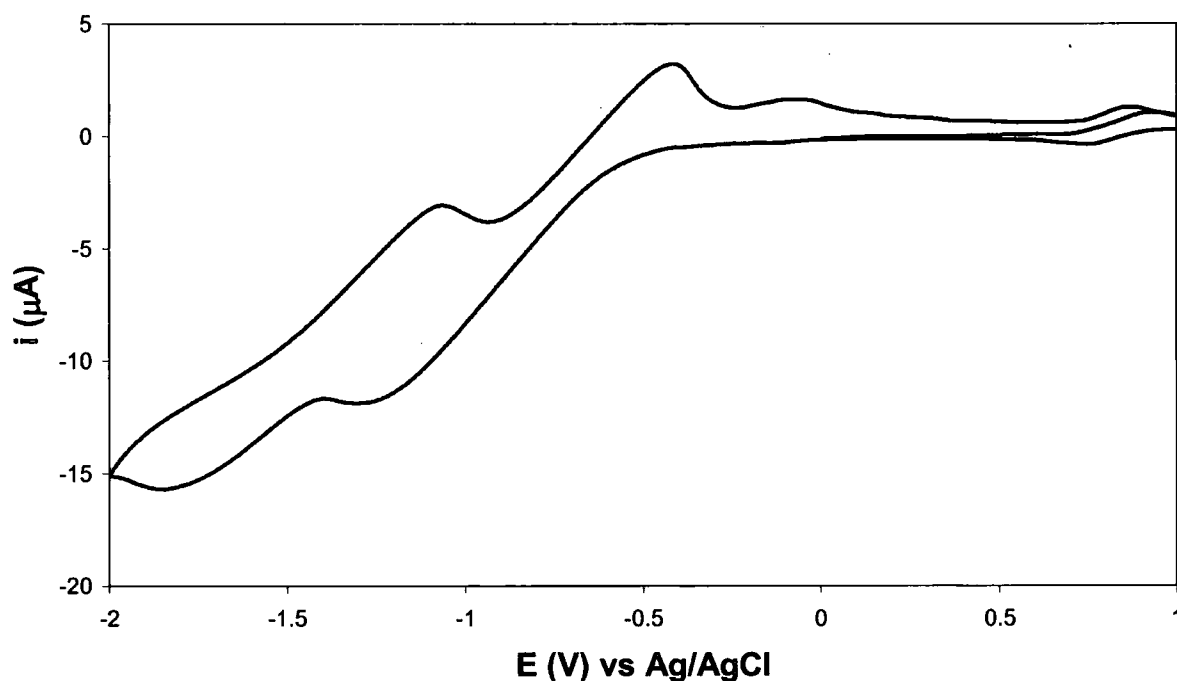


Figure 5. Cyclic voltammetry of **84** in *o*-dichlorobenzene.

The CV was disappointing in that the oxidation and the coupled reduction process of the donor was less clear than for **82**, and two completely irreversible waves corresponding to the C_{60} part were observed (E_1^{ox} -0.40 V, E_2^{ox} -1.05 V). We faced the same problem of diffusion of the species, which we attempted to solve by addition of acetonitrile, but unfortunately this did not lead to any improved reversibility or resolution.

The cyclic voltammetry of the bis-adduct **85** was performed under the same conditions as for **84** (Figure 6).

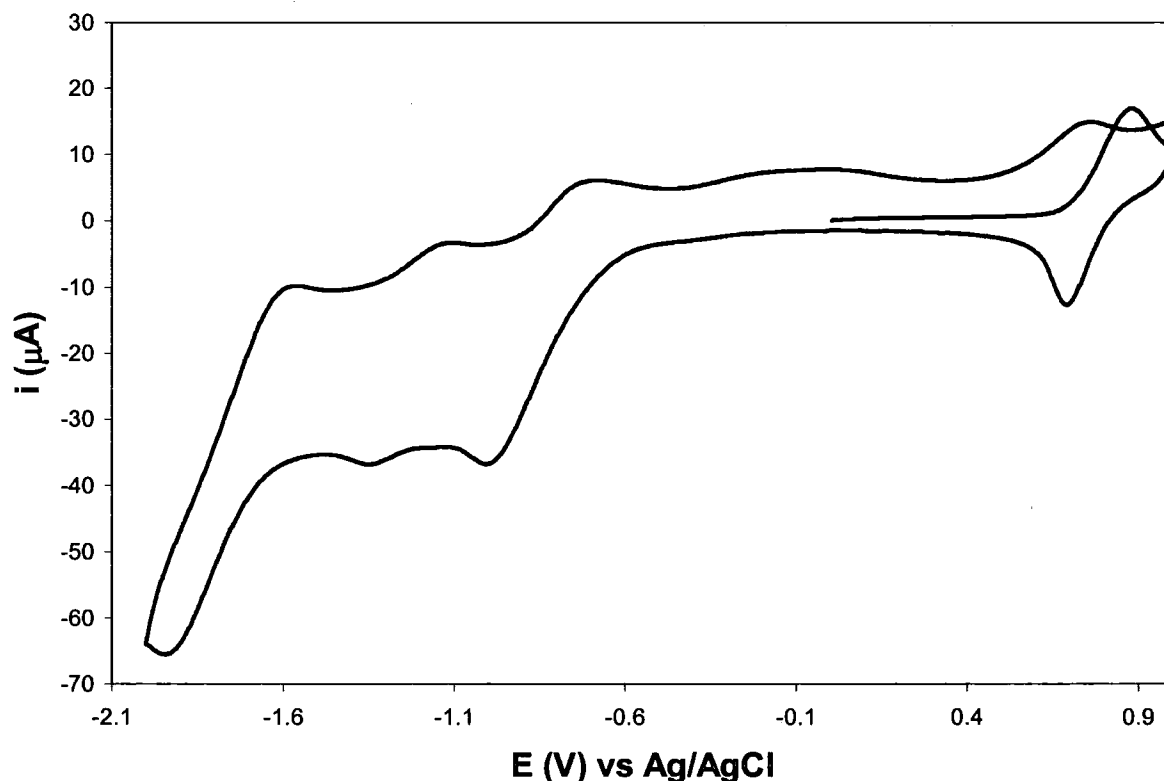


Figure 6. Cyclic voltammetry of **85** in *o*-dichlorobenzene.

We observed very clearly for **85** a single, irreversible, two-electron oxidation process occurring for the donor (E^{ox} 0.88 V), and three different waves, all irreversible, for the reduction of the acceptor part (E_1^{ox} -0.70 V, E_2^{ox} -1.12 V, E_3^{ox} -1.57 V). In this case, the problem of the diffusion of species seemed to be less important than in the previous experiments according to the appearance of the CV, but it was still present. This can be explained by a different conformation adopted by the molecule **85**, which leads to less blocking of the working electrode.

These electrochemical behaviours are unexpected; indeed, several complexes of C_{60} and anthracene-TTF attached covalently to TTF derivatives have been reported to

possess very clear cyclic voltammetric properties, for both the donor and the acceptor parts [8, 10, 13, 26].

The UV/Vis data for compounds **84** and **85** provided essentially the same information as for compounds **82** and **83**. We can see the absorbance of the donor at 374 nm, and the typical bands of the C₆₀ at 433 nm, confirming that mono addition has occurred, and another band at 704 nm (Figure 7).

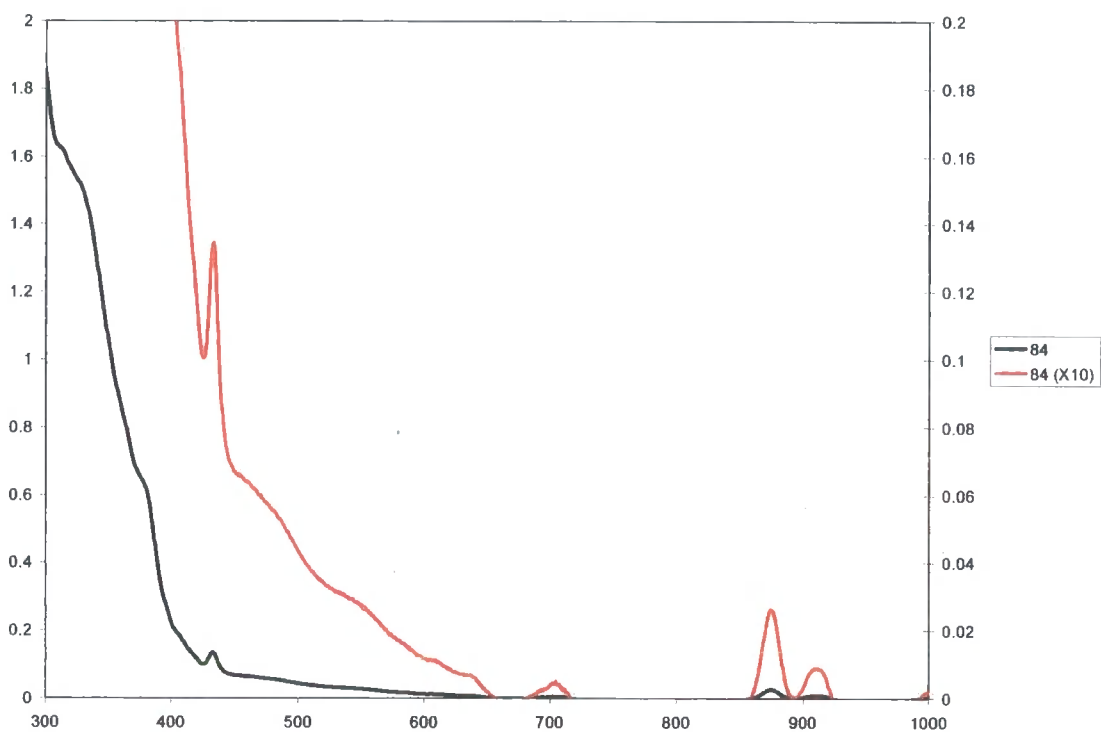


Figure 7. UV/vis absorption spectrum of **84**.

On the spectrum of the bis-adduct **85** (Figure 8), we can still see the absorbance of the donor at 379 nm, and again the band at 714 nm for the acceptor, with the band at 433 nm having disappeared.

For these two compounds, we observed additionally the two further bands at 874 and 911 nm for the same reasons as before we attributed them to inter- or intra-molecular charge transfer.

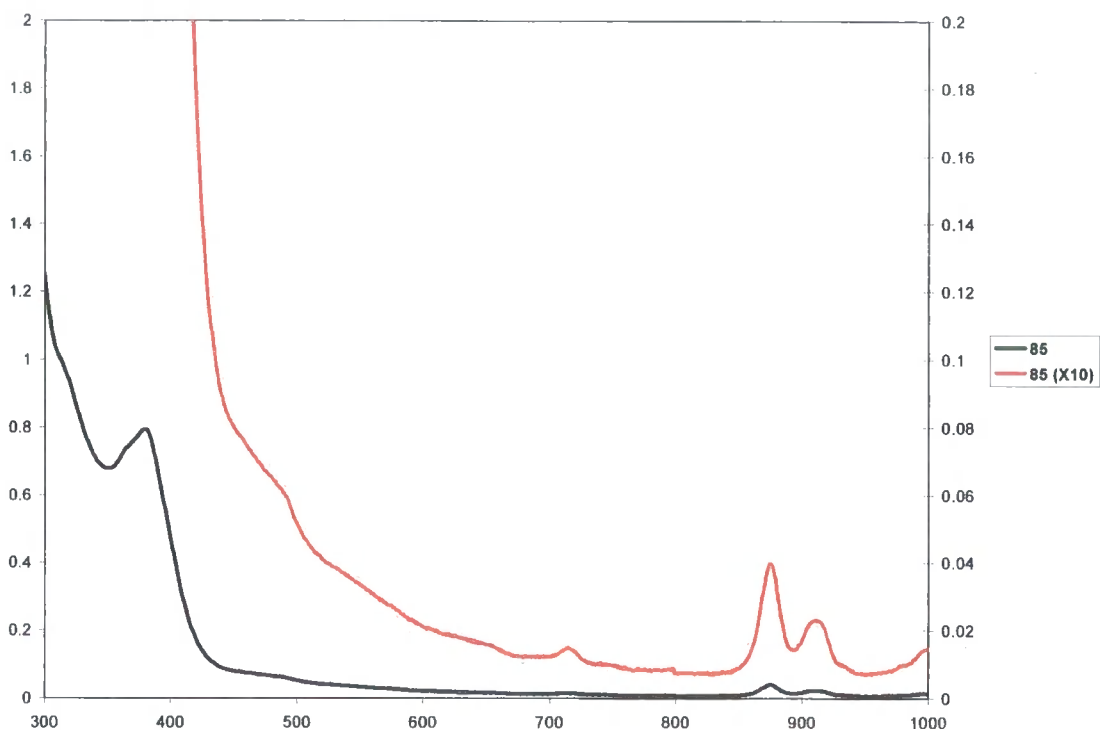


Figure 8. UV/vis absorption spectrum of **85**.

As the cyclic voltammetries of these C_{60} adducts were not very clear, no further studies on their properties, such as spectroelectrochemistry or photophysical measurements properties were carried out.

CONCLUSION:

We succeeded in synthesising aldehyde derivative **81**, and by using this reagent and aldehyde derivative **56**, we have been able to attach the 1,3-dithiol-2-ylidene)thioxanthene system covalently, via a pyrrolidine ring, to the C₆₀ unit to form novel donor-acceptor diads.

In both cases, we isolated the mono- and bis-adducts (the latter presumably as a mixture of regioisomers) but unfortunately, their electrochemical properties were not as clean and well-resolved as we had hoped, due to problems of aggregation at the working electrode, which is difficult to control because of the low solubility of the species.

However, NMR and UV/vis spectroscopic data were entirely consistent with the proposed structures of these adducts, and enabled us to identify and characterise them. Due to the inconclusive solution electrochemical data we did not perform any more detailed physical studies of these compounds.

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CHAPTER FIVE

EXPERIMENTAL DETAILS

General Equipment and Procedures

^1H and ^{13}C NMR spectra were obtained on Oxford 200, Varian Unity 300 and Varian VXR 400S spectrometers operating at 199.992 (^1H) and 50.293 (^{13}C), 299.908 (^1H) and 75.420 (^{13}C), and 400.0 (^1H) and 100.6 (^{13}C) MHz, respectively.

Mass spectra were recorded on a Micromass Autospec spectrometer operating at 70eV.

Infra-red spectra were recorded using KBr disks on a Perkin Elmer 1600 FTIR, spectrometer operated from a Grams Analyst 1600.

Electronic absorption spectra were obtained using a Perkin Elmer II UV-vis spectrophotometer operating with 1 ml quartz cells.

Melting points were obtained on a Philip Harris melting point apparatus and are uncorrected. Elemental analyses were obtained on an Exeter Analytical Inc. CE-440 elemental analyser. The EPR spectra were recorded on X-band Bruker spectrometer (ESP-300).

Cyclic voltammetric data were measured with IR compensation using a BAS CV50 electrochemical analyser. The experiments were carried out 3 ml of a *ca.* 10^{-4} M solution of the compound in DCM, or THF containing 0.1 M tetrabutylammonium hexafluorophosphate as the supporting electrolyte, at scan rate 100 mV/s. The oxidation potentials were measured *versus* a platinum wire quasi-reference electrode and referenced *versus* Ag/AgCl, unless otherwise stated.

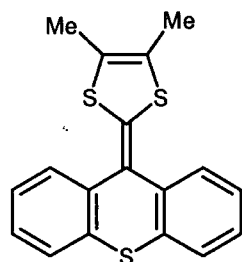
Column chromatography was carried out using Merck silica gel (70-230 mesh) and solvents were distilled prior to use in column chromatography.

Experimental Procedure for Chapter Two

General procedure for Horner-Wadsworth-Emmons reaction:

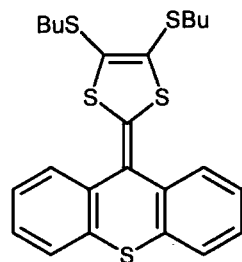
To a stirred solution of the phosphonate ester **35** in dry THF under N₂ at -78°C, lithium diisopropylamide monotetrahydrofuran (ca. 1.5 M in hexane) was added and the mixture was stirred for 30 min. Thioxanthen-9-one **34** dissolved in THF was added slowly and the mixture was left to warm to room temperature overnight. Solvents were removed *in vacuo* and the residue was purified by chromatography on silica gel.

9-(4,5-Dimethyl-1,3-dithiol-2-ylidene)thioxanthene (33a)



Following the general procedure **35a** (4.71 g, 19.38 mmol), LDA (14.20 ml, 21.32 mmol), and thioxanthen-9-one **34** (4.10 g, 19.38 mmol) were stirred overnight. After evaporation and chromatography on silica (eluent, dichloromethane/hexane: 1:1), recrystallisation from acetonitrile gave compound **33a** (3.17 g, 50%), yellow needles, mp: 210-212°C. ¹H NMR (CDCl₃): δ (ppm) 7.61 (d, 2H, *J*=4 Hz), 7.40 (d, 2H, *J*=4 Hz), 7.29 (dd, 2H, *J*=4 Hz, *J*=6 Hz), 7.19 (dd, 2H, *J*=4 Hz, *J*=6 Hz), 1.9 (s, 6H, CH₃). ¹³C NMR (CDCl₃): δ 137.02, 136.01, 132.23, 127.06, 126.73, 126.39, 125.83, 121.01, 120.61, 13.13. MS (EI): *m/z* (%): 326 [M⁺] (100). UV/Vis (CHCl₃): λ_{max} (lgε) 384.2 (0.383) nm. C₁₈H₁₄S₃ (326.03): calcd, C 66.21; H 4.32; found C 66.06, H 4.25.

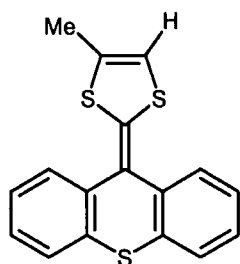
9-(4,5-Dithiobutyl-1,3-dithiol-2-ylidene)thioxanthene (33b)



Following the general procedure **35b** (0.73 g, 1.88 mmol), LDA (1.37 ml, 2.06 mmol), and thioxanthen-9-one **34** (0.40 g, 1.88 mmol) were stirred overnight. After evaporation and chromatography on silica (eluent, dichloromethane/hexane: 1:9), recrystallisation from

hexane gave compound **33b** (0.30 g, 34%), yellow solid, mp: 93-95°C. ^1H NMR (CDCl_3): δ (ppm) 7.56 (d, 2H, $J=4$ Hz), 7.44 (d, 2H, $J=4$ Hz), 7.32 (dd, 2H, $J=4$ Hz, $J=6$ Hz), 7.24 (dd, 2H, $J=4$ Hz, $J=6$ Hz), 2.78 (m, 4H), 1.61 (m, 4H), 1.42 (m, 4H), 0.92 (t, 6H, $J=3.99$ Hz). ^{13}C NMR (CDCl_3): δ 136.59, 134.00, 132.56, 127.37, 127.22, 126.81, 126.35, 126.31, 123.23, 36.12, 31.94, 21.89, 13.84. MS (EI): m/z (%): 474 [M^+] (100). UV/Vis (CHCl_3): λ_{max} (lg ϵ) 377 (0.315) nm. $\text{C}_{24}\text{H}_{26}\text{S}_5$ (474.06): calcd, C 60.71; H 5.52; found C 60.83, H 5.53.

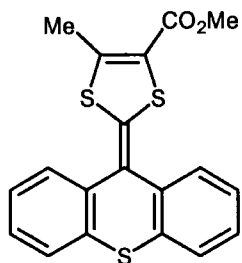
9-(4-Methyl-1,3-dithiol-2-ylidene)thioxanthene (33c)



Following the general procedure **35c** (3.75 g, 16.37 mmol), LDA (12 ml, 18.01 mmol), and thioxanthene-9-one **34** (3.47 g, 16.37 mmol) were stirred overnight. After evaporation and chromatography on silica (eluent, dichloromethane/hexane: 1:1), recrystallisation from ethyl acetate gave compound **33c** (2.45 g, 48%), yellow crystals, mp:

140-142°C. ^1H NMR (CDCl_3): δ (ppm) 7.65 (dd, 2H, $J=4$ Hz, $J=6$ Hz), 7.40 (d, 2H, $J=4$ Hz), 7.28 (m, 2H), 7.19 (dd, 2H, $J=4$ Hz, $J=6$ Hz), 5.79 (s, 1H), 2.0 (s, 3H, CH_3). ^{13}C NMR (CDCl_3): δ 139.12, 137.29, 136.90, 132.23, 132.20, 129.28, 126.95, 126.94, 126.86, 125.91, 121.83, 110.88, 15.97. MS (EI): m/z (%): 312 [M^+] (100). UV/Vis (CHCl_3): λ_{max} (lg ϵ) 378.8 (0.365) nm. $\text{C}_{17}\text{H}_{12}\text{S}_3$ (312.01): calcd, C 65.34; H 3.87; found C 65.31, H 3.79.

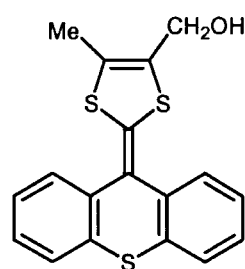
9-(4-Methoxycarbonyl-1,3-dithiol-2-ylidene)thioxanthene (36)



To a stirred solution of compound **33c** (2.40 g, 7.69 mmol) in dry THF under N_2 at -78°C , was added lithium diisopropylamide monotetrahydrofuran (ca. 1.5 in hexane) (5.64 ml, 8.46 mmol). The reaction mixture was stirred for 2 h. Methyl chloroformate (1.18 ml, 15.38 mmol) was added and the mixture was stirred and left to warm to room temperature overnight. The solvents were removed *in vacuo* and the

residue was purified by chromatography on silica (eluent, dichloromethane), recrystallisation from ethyl acetate gave compound **36** (1.90 g, 67%), orange crystals, mp: 206-207°C. ¹H NMR (CDCl₃): δ (ppm) 7.60 (dd, 2H, *J*=4 Hz, *J*=6 Hz), 7.44 (dd, 2H, *J*=4 Hz, *J*=6 Hz), 7.32 (m, 2H), 7.24 (dd, 2H, *J*=4 Hz, *J*=6 Hz), 3.78 (s, 3H, CO₂CH₃), 2.38 (s, 3H, CH₃). ¹³C NMR (CDCl₃): δ 160.55, 145.39, 136.16, 132.37, 132.16, 127.22, 127.18, 127.03, 126.94, 126.59, 126.43, 126.12, 125.97, 122.97, 116.97, 52.18, 15.51. IR (KBr) 3021, 2922, 2851, 1700, 1653, 1610, 1509, 1443, 1420, 1265, 1018, 908, 833, 675, 553 cm⁻¹. MS (EI): *m/z* (%): 370 [M⁺] (100). UV/Vis (CHCl₃): λ_{max} (lgε) 368.2 (0.462) nm. C₁₉H₁₄O₂S₃ (370.02): calcd, C 61.59; H 3.81; found C 61.31, H 3.74.

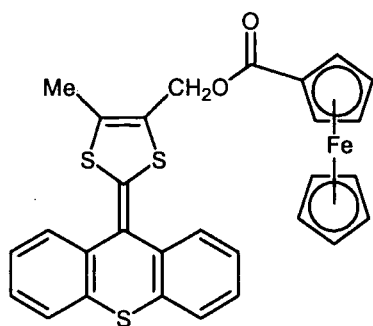
9-(4-Hydroxymethyl-1,3-dithiol-2-ylidene)thioxanthene (37)



To a stirred solution of compound **36** (1.50 g, 4.05 mmol) in dry THF under N₂ at -78°C, was added lithium aluminium hydride (0.61 g, 16.19 mmol) and the resultant mixture was stirred for 2 h at room temperature. After adding dropwise wet sodium sulphate (in excess), the reaction was stirred for 30 min. The reaction was filtered through Celite while washing with methanol. After evaporation of the

filtrate, the residue was recrystallised from ethyl acetate to give **37** (1.09 g, 79%), yellow crystals, mp: 209-212°C. ¹H NMR (CDCl₃): δ (ppm) 7.57 (dd, 2H, *J*=4 Hz, *J*=6 Hz), 7.47 (dd, 2H, *J*=4 Hz, *J*=6 Hz), 7.36 (dd, 2H, *J*=4 Hz, *J*=6 Hz), 7.28 (dd, 2H, *J*=4 Hz, *J*=6 Hz), 5.34 (t, 1H, *J*=6 Hz, OH), 4.17 (d, 2H, *J*=7.6 Hz, CH₂O), 1.93 (s, 3H, CH₃). ¹³C NMR (DMSO) 136.21, 135.93, 131.01, 127.97, 127.12, 126.90, 126.31, 121.93, 120.55, 55.97, 12.71. MS (EI): *m/z* (%): 342 [M⁺] (100). UV/Vis (CHCl₃): λ_{max} (lgε) 376 (0.314) nm. C₁₈H₁₄OS₃ (342.02): calcd, C 63.12; H 4.12; found C 63.07, H 4.20.

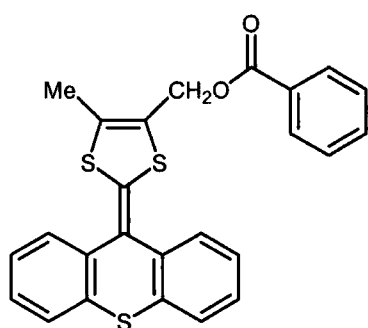
9-(4-Ferrocene-carbonyloxymethyl-1,3-dithiol-2-ylidene)thioxanthene (39)



To a stirred mixture of compound **37** (0.30 g, 0.87 mmol) and ferrocene carbonyl chloride **38** (0.21 g, 0.87 mmol) in dry dichloromethane under N₂, was added triethylamine (0.48 ml, 3.5 mmol), the mixture was stirred for 6 h at room temperature. Then the solvents were removed *in vacuo* and the residue was chromatographed on silica (eluent, dichloromethane) and then recrystallisation from

hexane gave compound **39** (0.35 g, 72%), orange solid, mp: 119-121°C. ¹H NMR (CDCl₃): δ (ppm) 7.60 (dd, 2H, *J*=4 Hz, *J*=6 Hz), 7.37 (dd, 2H, *J*=4 Hz, *J*=6 Hz), 7.26 (dd, 2H, *J*=4 Hz, *J*=6 Hz), 7.17 (dd, 2H, *J*=4 Hz, *J*=6 Hz), 4.89 (s, 2H), 4.79 (s, 2H), 4.40 (s, 2H), 4.15 (s, 5H), 2.1 (s, 3H, CH₃). ¹³C NMR (CDCl₃): δ 171.30, 136.70, 134.88, 132.28, 128.40, 127.09, 126.97, 126.45, 125.88, 122.44, 122.11, 71.51, 70.23, 70.19, 69.83, 57.70, 13.53. MS (EI): *m/z* (%): 554 [M⁺] (9.3), 230 [FeCO₂] (100). UV/Vis (CHCl₃): λ_{max} (lgε) 373(0.1378) nm. C₁₈H₁₄FeO₂S₃ (554.01): calcd, C 62.81; H 4.00; found C 63.01, H 4.20.

9-(4-Phenylcarbonyloxymethyl-1,3-dithiol-2-ylidene)thioxanthene (**40**)

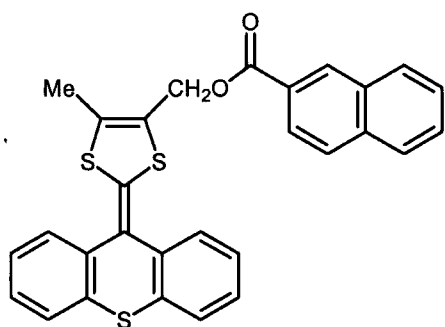


To a stirred mixture of compound **37** (0.202 g, 0.591 mmol) with benzoyl chloride (13.73 ml, 1.18 mmol) in dry dichloromethane under N₂, was added triethylamine (16.48 ml, 1.18 mmol), the mixture was stirred for 6 h at room temperature. Then the solvents were removed *in vacuo* and the residue was chromatographed on silica (eluent, dichloromethane), and then recrystallisation from

acetonitrile gave compound **40** (227.3 mg, 86%), yellow solid, mp: 153-155°C. ¹H NMR (CDCl₃): δ (ppm) 8.02 (d, 2H, *J*=8 Hz), 7.6 (d, 2H, *J*=8 Hz), 7.59 (m, 1H), 7.44 (d, 2H, *J*=8 Hz), 7.42 (d, 2H, *J*=8 Hz), 7.29 (dd, 2H, *J*=4 Hz, *J*=6 Hz), 7.19 (dd, 2H, *J*=4 Hz, *J*=6 Hz), 4.98 (s, 2H, CH₂O), 2.09 (s, 3H, CH₃). ¹³C NMR (CDCl₃): δ 133.78, 130.05, 128.66, 127.19, 126.71, 126.12, 121.56, 120.48, 58.30, 13.82. MS (EI): *m/z* (%): 446 [M⁺] (5.99),

84 [M^+ -362] (100). UV/Vis (CHCl_3): λ_{max} (lg ϵ) 374(1.92) nm. $\text{C}_{29}\text{H}_{20}\text{O}_2\text{S}_3$ (446.05): calcd, C 67.23; H 4.06; found C 67.29, H 4.12.

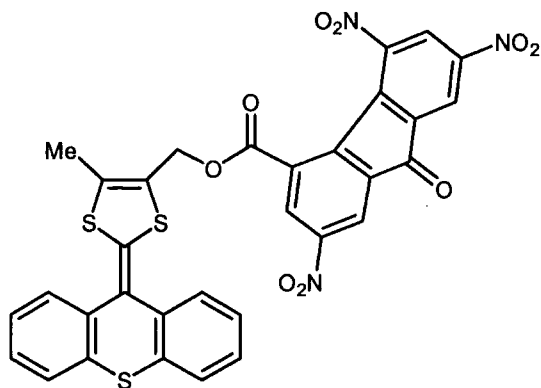
9-(4-(2-Naphthyl)carbonyloxymethyl-1,3-dithiol-2-ylidene)thioxanthene (41)



To a stirred mixture of compound **37** (0.2 g, 0.58 mmol) with 2-naphthoyl chloride (0.111 g, 0.58 mmol) in dry dichloromethane under N_2 , was added triethylamine (0.08 ml, 0.58 mmol), the mixture was stirred for 6 h at room temperature. Then the solvents were removed *in vacuo* and the residue was chromatographed on silica (eluent, chloroform) and

then recrystallisation from acetonitrile gave compound **41** (238 mg, 82%), yellow solid, mp: 185-187°C. ^1H NMR (CDCl_3): δ (ppm) 8.6 (s, 1H), 8.00 (dd, 2H, $J=4$ Hz, $J=6$ Hz), 7.87 (d, 2H, $J=8$ Hz), 7.61 (d, 2H, $J=8$ Hz), 7.59 (m, 2H), 7.40 (d, 2H, $J=8$ Hz), 7.29 (dd, 2H, $J=4$ Hz, $J=6$ Hz), 7.19 (dd, 2H, $J=4$ Hz, $J=6$ Hz), 5.05 (s, 2H, CH_2O), 2.12 (s, 3H, CH_3). ^{13}C NMR (CDCl_3): δ 166.56, 136.99, 135.89, 135.14, 132.65, 132.55, 132.47, 131.70, 129.68, 129.5, 128.67, 128.48, 128.01, 127.27, 127.24, 127.21, 126.94, 126.77, 126.73, 126.31, 126.19, 125.49, 122.29, 120.75, 58.83, 13.81. MS (EI) : m/z (%) : 496 [M^+] (7.20), 77 [benzene] (100). UV/Vis (CHCl_3): λ_{max} (lg ϵ) 375(1.89) nm. $\text{C}_{29}\text{H}_{20}\text{O}_2\text{S}_3$ (496.06): calcd, C 70.13; H 4.06; found C 69.87, H 3.88.

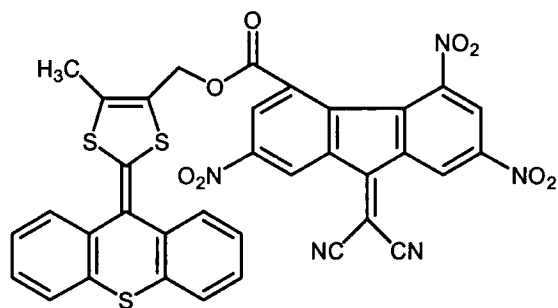
9-[4-(2,5,7-Trinitrofluoren-9-one)carbonyloxymethyl-1,3-dithiol-2-ylidene]thioxanthene (43)



To a stirred solution of compound **37** (0.50 g, 1.45 mmol) in dry THF under N_2 at -100°C , was added *n*-butyllithium (0.91 ml, 1.45 mmol), the solution was stirred for 30 min. Then 2,5,7 trinitro-4-chlorocarbonyl

fluoren-9-one **42** (0.55 g, 1.45 mmol) was added very slowly and then the solution was warmed to 20°C and stirred overnight. After evaporation, the residue was taken up in dichloromethane, and washed several times with water, and then dried over magnesium sulfate. The residue was purified by chromatography on silica gel with chloroform as the eluent to afford compound **43** (0.20 g, 20%), black solid, mp: 162-163°C. ¹H NMR (CDCl₃): δ (ppm) 8.92 (s, 1H), 8.85 (s, 1H), 8.79 (s, 1H), 8.75 (s, 1H), 7.58 (dd, 2H, *J*=4 Hz, *J*=6 Hz), 7.38 (dd, 2H, *J*=4 Hz, *J*=6 Hz), 7.28 (dd, 2H, *J*=4 Hz, *J*=6 Hz), 7.20 (dd, 2H, *J*=4 Hz, *J*=6 Hz), 5.03 (q, 2H, CH₂O), 2.12 (s, 3H, CH₃). ¹³C NMR (CDCl₃): δ 184.79, 164, 149.63, 149.33, 146.50, 143.41, 139.60, 138.75, 137.74, 136.51, 136.41, 133.97, 132.17, 130.89, 127.12, 126.98, 126.49, 126.02, 125.27, 122.57, 122.53, 122, 118.59, 60.53, 13.60. MS (ES): *m/z* (%): 682.4 [M⁺] (100). UV/Vis (CHCl₃): λ_{max} (lgε) 361(0.223) nm. C₃₂H₁₇N₃O₉S₃ (683.01): calcd, C 56.22; H 2.51, N 6.15; found C 55.95, H 2.55, N 5.89.

9-[4-(2,5,7-Trinitrofluoren-9-dicyanomethylene)carbonyloxymethyl-1,3-dithiol-2-ylidene]thioxanthene (44**)**

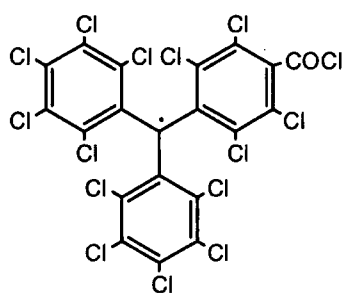


To a stirred solution of compound **43** (0.03 g, 0.043 mmol) dissolved in dry DMF (ca 2 ml) under N₂ at room temperature, was added malononitrile (14.48 mg, 0.21 mmol), the solution was stirred overnight.

The solvent was removed *in vacuo*, and methanol was added and the mixture was placed at 5°C for 30 min and the solid was filtered and washed with methanol to give compound **44** (16 mg, 51%), dark green solid, mp: > 300°C. ¹H NMR (CDCl₃): δ (ppm) 9.64 (dd, 2H, *J*=4 Hz, *J*=8 Hz), 8.93 (dd, 2H, *J*=4 Hz, *J*=8 Hz), 7.58 (dd, 2H, *J*=4 Hz, *J*=6 Hz), 7.4 (dd, 2H, *J*=4 Hz, *J*=6 Hz), 7.3 (dd, 2H, *J*=4 Hz, *J*=6 Hz), 7.22 (dd, 2H, *J*=4 Hz, *J*=6 Hz), 5.03 (q, 2H, CH₂O), 2.12 (s, 3H, CH₃). ¹³C NMR (CDCl₃): δ 163.94, 153.41, 149.47, 149.01, 147.01, 140.56, 138.90, 137.85, 137.10, 136.76, 136.65, 132.45, 132.19, 131.82, 130.66, 127.41, 127.25, 127.15,

126.78, 126.74, 126.25, 124.90, 124.10, 123.41, 122.95, 118.69, 111.67, 111.57, 60.91, 13.87. IR (KBr) 2370, 2343, 2231, 1741, 1636, 1540, 1458, 1344, 1314, 1146, 767, 694 cm^{-1} . MS (ES) : m/z (%): 730.4 [M^+] (100). UV/Vis (CHCl_3): λ_{max} (lg ϵ) 305(0.46), 358(0.38), 374(0.41) nm. $\text{C}_{35}\text{H}_{17}\text{N}_5\text{O}_8\text{S}_3$ (731.02): High Resolution MS: calcd: 731.0239; found: 731.0225.

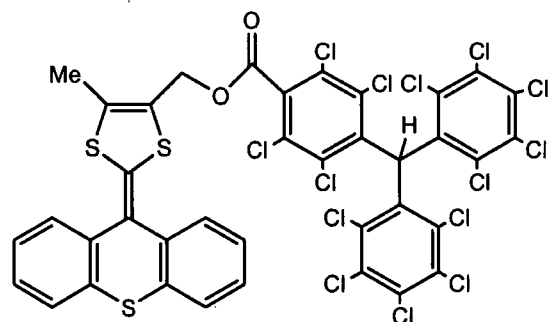
4-[bis(2,3,4,5,6-pentachlorophenyl)methyl]-2,3,5,6-tetrachlorobenzoic radical acid chloride (45)



A solution of 4-[bis(2,3,4,5,6-pentachlorophenyl)methyl]-2,3,5,6-tetrachlorobenzoic radical acid (53 mg, 0.068 mmol) in thionyl chloride (5 ml) was refluxed for 24 h. Evaporation of the solvent gave a residue which was passed through silica gel in chloroform, and recrystallised from a mixture of DCM/hexane, giving compound **45** (34 mg, 61%) as red

powder. IR (KBr) 1783, 1384, 1336, 1324, 771 cm^{-1} .

4-(Bis-pentachlorophenyl-methyl)-2,3,5,6-tetrachloro-benzoate 5-methyl-2-thioxanthen-9-ylidene-1,3-dithiol-4-yl (48)

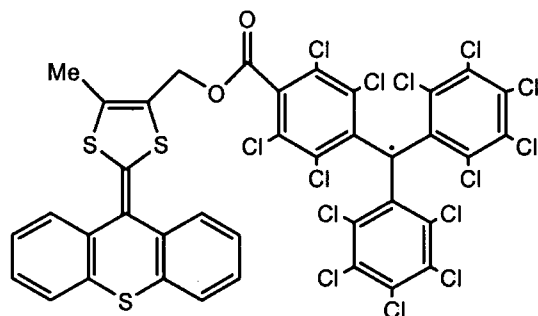


To a stirred solution of compound **37** (27 mg, 0.072 mmol) in dry DCM, under N_2 , at room temperature, was added 4-dimethylaminopyridine (19 mg, 0.145 mmol). The reaction mixture was stirred for 30 min at 20°C . A solution of 4-[bis(2,3,4,5,6-

pentachlorophenyl)methyl]-2,3,5,6-tetrachlorobenzoic acid chlorid **47** (122 mg, 0.145 mmol) dissolved in DCM was added to the mixture, which was stirred overnight. The solvent was removed *in vacuo* and the residue was chromatographed on silica (eluent, chloroform) to give compound **48** (70 mg, 81%), red powder. ^1H NMR (CDCl_3): δ (ppm) 7.60 (m, 2H), 7.44 (d, 2H, $J=8$ Hz), 7.27 (m, 4H), 7 (s, 1H, CH), 3.52 (s, 2H), 2.20 (s,

3H, CH₃). MS (EI): m/z (%): 1095 [M⁺] (42.65), 1094 [M⁺-H] (100). IR (KBr) 3057, 2922, 2851, 1739, 1458, 1434, 1360, 1341, 809 cm⁻¹.

4-(Bis-pentachlorophenyl-methyl)-2,3,5,6-tetrachloro-benzoic radical acid 5-methyl-2-thioxanthen-9-ylidene-1,3-dithiol-4-ylmethyl ester (46)

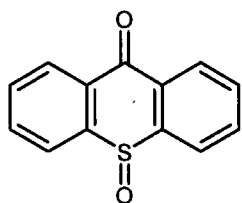


To a stirred solution of compound **37** (16 mg, 0.04 mmol) in dry DCM, under N₂, at room temperature, was added dimethylaminopyridine (10 mg, 0.08 mmol). The reaction mixture was stirred for 30 min at 20°C. A solution of 4-[bis(2,3,4,5,6-

pentachlorophenyl)methyl]-2,3,5,6-tetrachlorobenzoic radical acid chloride **45** (34 mg, 0.04 mmol) dissolved in DCM was added to the mixture, which was stirred overnight. The solvent was removed *in vacuo* and the residue was chromatographed on silica (eluent, DCM/hexane, 1:1). The product obtained was dissolved in ethyl acetate, and the solution was filtered. The filtrate was evaporated to give compound **46** (40 mg, 78%), red powder, mp: 117-119°C. IR (KBr) 3057, 2923, 2852, 1746, 1458, 1434, 1335, 1324, 817 cm⁻¹, UV/Vis (CHCl₃): λ_{max} (lgε) 283(0.55), 368(0.65), 383(0.94) nm, C₃₈H₁₃Cl₁₄O₂S₃ (1086.57): calcd, C 41.72; H 1.20; found C 41.76, H 1.22.

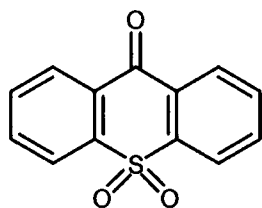
Alternative preparation of Radical 46. To a stirred solution of compound **48** (70 mg, 0.07 mmol) in dry THF (30 mL) at 20 °C, was added tetrabutylammonium hydroxide (19.8 mg, 0.076 mmol). The reaction mixture was stirred for 2 h at 20 °C. *Para*-chloranil (26 mg, 0.104 mmol) was added and the mixture was stirred for 1 h at 20 °C. The solvent was removed *in vacuo* and the residue was purified by chromatography on silica (eluent, hexane/dichloromethane 1:1 (v/v)) to give compound **46** (13 mg, 6%) identical with the sample prepared above.

10-Oxo-10H-thioxanthen-9-one (49)



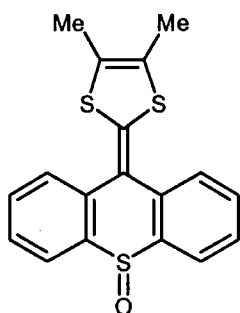
To a stirred solution of thioxanthen-9-one **34** (1 g, 4.71 mmol) in hexafluoro-2-propanol at 20°C, was added hydrogen peroxide (0.32 g, 9.43 mmol) and the mixture was refluxed for 15 min.. The hydrogen peroxide was quenched by addition of a saturated aqueous solution of sodium sulfite. Then water was added to the mixture; the precipitate was filtered and chromatographed on silica (eluent, hexane/ diethylether 1:1) to afford compound **49** (0.146 g, 13.5%), yellow crystals, mp: 118-120°C. ¹H NMR (CDCl₃): δ (ppm) 8.39 (dd, 2H, *J*=4 Hz, *J*=6 Hz), 8.19 (dd, 2H, *J*=4 Hz, *J*=6 Hz), 7.86 (t, 2H, *J*=4 Hz), 7.74 (t, 2H, *J*=4 Hz). ¹³C NMR (CDCl₃): δ 180.11, 145.17, 134.01, 131.65, 129.64, 128.83, 127.26. MS (EI): *m/z* (%): 228 [*M*⁺] (100). UV/Vis (CHCl₃): λ_{max} (lgε) 327 (0.914) nm. C₁₃H₈O₂S (228.02): calcd, C 68.40; H 3.53; found C 68.25, H 3.50.

10,10-Dioxo-10H-thioxanthen-9-one (50)



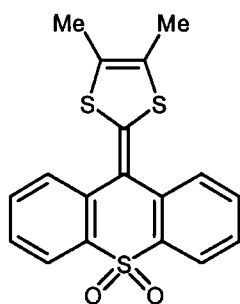
To a stirred solution of thioxanthen-9-one **34** (1 g, 4.71 mmol) in acetic acid at 20°C, was added hydrogen peroxide (0.16 g, 4.71 mmol) and the mixture was refluxed for 2 h, then cooled to 20 °C to afford a precipitate which was filtered and washed with hexane to afford compound **50** (0.938 g, 81%), yellow crystals, mp: 179-180°C. ¹H NMR (CDCl₃): δ (ppm) 8.35 (dd, 2H, *J*=4 Hz, *J*=6 Hz), 8.19 (dd, 2H, *J*=4 Hz, *J*=6 Hz), 7.89 (t, 2H, *J*=4 Hz), 7.80 (t, 2H, *J*=4 Hz). ¹³C NMR (CDCl₃): δ 178.60, 141.17, 134.91, 133.49, 130.90, 129.42, 123.79. MS (EI): *m/z* (%): 244 [*M*⁺] (53.32), 196 [*M*⁺-3O] (100). UV/Vis (CHCl₃): λ_{max} (lgε) 383 (0.253) nm. C₁₃H₈O₃S (244.02): calcd, C 63.92; H 3.30; found C 63.69, H 3.29.

9-(4,5-Dimethyl-1,3-dithiol-2-ylidene)-thioxanthene 10-oxide (51)



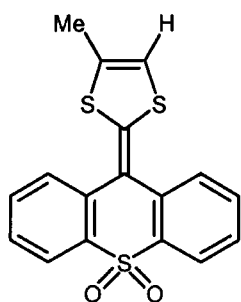
Following the general procedure for Wittig reaction, phosphonium salt **35a** (0.155 g, 0.64 mmol), LDA (0.47 ml, 0.7 mmol), and compound **49** (0.146 g, 0.64 mmol) were stirred overnight. After evaporation and chromatography on silica (eluent, dichloromethane), recrystallisation from ethyl acetate gave compound **51** (0.03 g, 13.5%), yellow crystals, mp: 235-237°C. ^1H NMR (CDCl_3): δ (ppm) 7.84 (d, 2H, $J=4$ Hz), 7.73 (d, 2H, $J=4$ Hz), 7.40 (m, 4H), 2.09 (s, 6H, CH_3). ^{13}C NMR (CDCl_3): δ 145.18, 134.01, 132.14, 131.66, 129.68, 129.64, 128.84, 127.74, 127.27, 126.50, 123.71, 121.53, 29.95, 13.43. MS (EI): m/z (%): 342 [M^+] (100). UV/Vis (CHCl_3): λ_{max} (lg ϵ) 396 (0.209) nm. $\text{C}_{18}\text{H}_{14}\text{OS}_3$ (342.02): High Resolution MS: calcd: 342.021 found: 342.022.

9-(4,5-Dimethyl-1,3-dithiol-2-ylidene)-thioxanthene 10,10-dioxide (**52**)



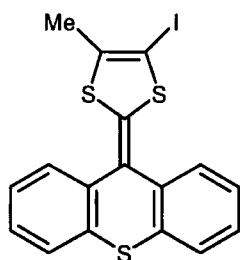
Following the general procedure for Wittig reaction, phosphonium salt **35a** (1 g, 4.11 mmol), LDA (2.82 ml, 4.52 mmol), and compound **50** (0.938 g, 4.11 mmol) were stirred overnight. After evaporation and chromatography on silica (eluent, dichloromethane), recrystallisation from ethyl acetate gave compound **52** (0.148 g, 10%), yellow crystals, mp: 243-244°C. ^1H NMR (CDCl_3): δ (ppm) 8.06 (d, 2H, $J=8$ Hz), 7.91 (d, 2H, $J=8$ Hz), 7.55 (t, 2H, $J=4$ Hz), 7.41 (t, 2H, $J=4$ Hz), 2.05 (s, 6H, CH_3). ^{13}C NMR (CDCl_3): δ 144.70, 138.58, 134.88, 132.04, 127.21, 127.05, 123.90, 122.09, 112.76, 109.99, 13.33. MS (EI): m/z (%): 358 [M^+] (100). UV/Vis (CHCl_3): λ_{max} (lg ϵ) 431 (0.282) nm. $\text{C}_{18}\text{H}_{14}\text{O}_2\text{S}_3$ (358.02): calcd, C 60.30; H 3.94; found C 60.35, H 3.92.

9-(4-Methyl-1,3-dithiol-2-ylidene)-thioxanthene 10,10-dioxide (**53**)



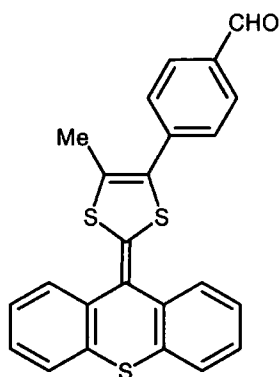
Following the general procedure for Wittig reaction, phosphonium salt **35c** (0.65 g, 2.66 mmol), LDA (1.9 ml, 2.93 mmol), and compound **50** (0.65 g, 2.66 mmol) were stirred overnight. After evaporation and chromatography on silica (eluent, dichloromethane), recrystallisation from ethyl acetate gave compound **53** (0.45 g, 49%), yellow powder, mp: 184-186°C. ¹H NMR (CDCl₃): δ (ppm) 8.06 (dd, 2H, *J*=2 Hz, *J*=4 Hz), 7.93 (q, 2H), 7.55 (m, 2H), 7.42 (t, 2H, *J*=4 Hz), 5.95 (s, 1H), 2.10 (s, 3H, CH₃). ¹³C NMR (CDCl₃): δ 138.82, 138.31, 134.91, 132.12, 130.67, 127.20, 127.08, 123.92, 113.61, 109.99, 16.53. MS (EI): *m/z* (%): 344 [M⁺] (100). UV/Vis (CHCl₃): λ_{max} (lgε) 428 (0.179) nm. C₁₇H₁₂O₂S₃ (344): calcd, C 59.27; H 3.51; found C 59.12, H 3.60.

9-(4-Iodo-5-methyl-1,3-dithiol-2-ylidene)-thioxanthene (**54**)



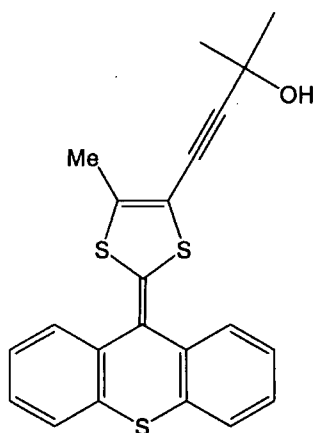
Phosphonate ester **35c** (0.13 g, 0.42 mmol) was dissolved in dry THF. The solution was cooled to -78°C and lithium diisopropylamide LDA (1.5 M in THF) (0.3 ml, 0.45 mmol) was added dropwise. The reaction was stirred at -78°C for 3 h then perfluorohexyl iodide (0.45 ml, 2.1 mmol) was added and the reaction was allowed to reach room temperature overnight. The mixture was concentrated *in vacuo* and the residue was dissolved in toluene; the extract was washed with water and dried (MgSO₄). Purification by column chromatography on silica (eluent, dichloromethane) followed by recrystallisation in ethyl acetate gave **54** (0.156 g, 85%), yellow needles, mp: 186-187°C. ¹H NMR (CDCl₃): δ (ppm) 7.46 (m, 2H), 7.35 (d, 2H, *J*=8 Hz), 7.19 (m, 4H), 1.96 (s, 3H, CH₃). ¹³C NMR (CDCl₃): δ 137.73, 136.62, 136.39, 132.52, 132.44, 130.35, 127.47, 127.45, 127.04, 126.76, 126.73, 136.36, 126.19, 123.02, 61.61, 19.19. MS (CI): *m/z* (%): 240 [M⁺-198] (100), 438 [M⁺] (84.02). UV/Vis (CHCl₃): λ_{max} (lgε) 378 (0.305) nm. C₁₇H₁₁OS₃ (437.97): calcd, C 46.58; H 2.53; found C 46.68, H 2.50.

4-(5-Methyl-2-thioxanthen-9-ylidene-1,3dithiol-4yl)-benzaldehyde (**56**)



Boronic acid **55** (0.35 g, 0.8 mmol), halide **54** (0.119 g, 0.8 mmol), and dichloro-bis-(triphenylphosphino)palladium catalyst (0.56 g, 0.8 mmol) were added sequentially to degassed THF, and the mixture was stirred for 30 min at room temperature. Degassed aqueous Na_2CO_3 solution 2 M was added and the reaction mixture was heated under nitrogen at 80°C for 3 days. The solvent was removed *in vacuo* and the residue was diluted in ethyl acetate, the organic layer was washed with brine and dried (MgSO_4). Purification by column chromatography (eluent, dichloromethane) gave compound **56** (0.244 g, 73%), yellow solid, mp: $233\text{--}235^\circ\text{C}$. ^1H NMR (CDCl_3): δ (ppm) 9.94 (s, 1H, *CHO*), 7.8 (d, 2H, $J=8$ Hz), 7.55 (t, 2H, $J=4$ Hz), 7.43 (d, 2H, $J=4$ Hz), 7.37 (t, 2H, $J=4$ Hz), 7.23 (m, 2H), 7.16 (m, 2H), 1.98 (s, 3H, CH_3). ^{13}C NMR (CDCl_3): δ 191.65, 138.60, 136.83, 135.84, 134.46, 132.53, 132.45, 130.20, 129.77, 127.33, 127.30, 126.79, 126.72, 126.26, 126.23, 125.99, 124.85, 122.36, 14.82. MS (CI): m/z (%): 152 [M^+-264] (100), 416 [M^+] (78.89). UV/Vis (CHCl_3): λ_{max} (lg ϵ) 381 (0.205) nm. $\text{C}_{24}\text{H}_{16}\text{OS}_3$ (416.04): calcd, C 69.20; H 3.87; found C 69.16, H 3.89.

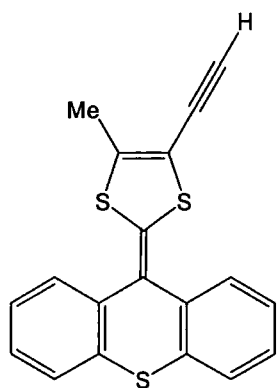
2-Methyl-4-(5-methyl-2-thioxanthene-9-ylidene-1,3-dithiol-4-yl)-but-3-yn-2-ol (**58**)



Dichloro-bis-(triphenylphosphino)palladium (0.010 g, 0.14 mmol), copper iodide (0.003 g, 0.014 mmol), and triethylamine (20 ml) were added sequentially to a solution of compound **54** (0.20 g, 0.45 mmol) and 2-methyl-3-butyn-2-ol **57** (0.1 ml, 0.9 mmol) in THF (10 ml). The mixture was stirred overnight at room temperature, and then heated for one hour at 50°C . The solvent was removed *in vacuo* and the residue was purified by column chromatography (eluent, dichloromethane) to give compound **58** (0.160 g, 89%), yellow powder, mp: $102\text{--}104^\circ\text{C}$. ^1H NMR (CDCl_3): δ (ppm) 7.56 (t, 2H, $J=4$ Hz), 7.41 (dd, 2H, $J=4$ Hz, $J=6$ Hz), 7.27 (m, 2H), 7.22 (t, 2H, $J=4$ Hz), 2.07 (s, 3H, CH_3), 1.90 (s, 1H, *OH*), 1.54 (s, 6H, CH_3). ^{13}C NMR (CDCl_3): δ 136.35, 135.16, 134.49, 132.23, 127.13, 127.04, 126.99,

126.52, 126.42, 125.98, 125.94, 122.93, 107.14, 99.96, 72.80, 65.68, 31.30, 15.21. MS (CI): m/z (%): 394 [M^+](100). UV/Vis ($CHCl_3$): λ_{max} (lg ϵ) 377 (0.317) nm. $C_{22}H_{18}OS_3$ (394.05): calcd, C 66.97; H 4.60; found C 66.86, H 4.58.

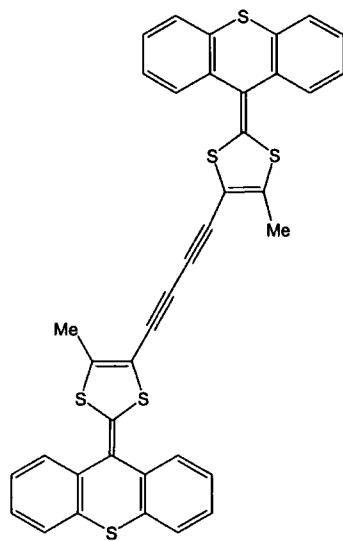
9-(4-Ethynyl-5-methyl-1,3-dithiol-2-ylidene)thioxanthene (59)



To a stirred solution of compound **58** (0.325 g, 0.82 mmol) in toluene/benzene 1:1, was added sodium hydroxide (0.066 g, 1.6 mmol), the mixture was refluxed overnight. The solvent was removed *in vacuo* and the residue was purified by column chromatography (eluent, dichloromethane) to give compound **59** (0.20 g, 72%), yellow powder, mp: 136-138°C. 1H NMR ($CDCl_3$): δ (ppm) 7.49 (m, 4H), 7.35 (m, 2H), 7.18 (m, 2H), 3.21 (s, 1H, $C\equiv H$), 2.04 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$): δ 137.81, 136.56,

132.56, 132.52, 132.45, 130.11, 127.41, 127.25, 127.19, 126.77, 126.67, 126.55, 126.26, 126.23, 126.19, 123.29, 107.08, 83.80, 29.94, 15.44. MS (CI): m/z (%): 212 [$M^+ - C\equiv CH$](100), 336 [M^+](65.52). UV/Vis ($CHCl_3$): λ_{max} (lg ϵ) 376 (0.122) nm. $C_{19}H_{12}S_3$ (336.01): calcd, C 67.82; H 3.59; found C 67.58, H 3.66.

1,4-Bis[(5-methyl-1,3-dithiol-2-ylidene)thioxanthene]butadiyne (60)

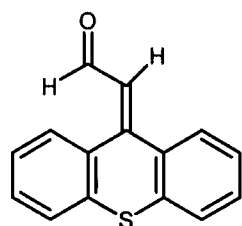


To a stirred solution of compound **59** (0.10 g, 0.29 mmol) in triethylamine/acetonitrile 2.5:1.5, was added at room temperature, dichloro-bis-(triphenylphosphino)palladium (6 mg, 3% mol,), copper iodide (1.6 mg, 3 mol%) and triphenylphosphine (8.3 mg, 9 mol%). The mixture was stirred overnight and formed a precipitate, which was filtered and washed with acetonitrile to give compound **60** (12mg, 6%), yellow powder, mp: >250°C. 1H NMR ($CDCl_3$): δ (ppm) 7.49 (m, 4H), 7.35 (m, 2H), 7.18 (m, 2H),

3.21 (s, 1H), 2.04(s, 3H). ^{13}C NMR (CDCl_3): δ 137.81, 136.56, 132.56, 132.52, 132.45, 130.11, 127.41, 127.25, 127.19, 126.77, 126.67, 126.55, 126.26, 126.23, 126.19, 123.29, 107.08, 83.80, 29.94, 15.44. MS (CI): m/z (%): 240 [$\text{M}^+ - 430$] (100), 670 [M^+] (25.59). UV/Vis (CHCl_3): λ_{max} (lg ϵ) 363(0.30), 386(0.30), 435(0.14) nm. $\text{C}_{38}\text{H}_{22}\text{S}_6$ (670.00): High Resolution MS: calcd: 670.0045; found: 670.0033.

Experimental Procedure for Chapter Three

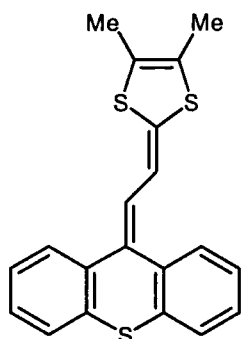
Thioxanthen-9-ylidene-acetaldehyde (65)



Phosphorus oxychloride (5.8 ml, 62.17 mmol) was added slowly to DMF (20 ml) cooled in an ice bath. To this mixture was slowly added a solution of methylenethioxanthene **64** (2.176 g, 10.36 mmol) in DMF (30 ml). The mixture was warmed to room temperature and was maintained at 60°C overnight. The reaction

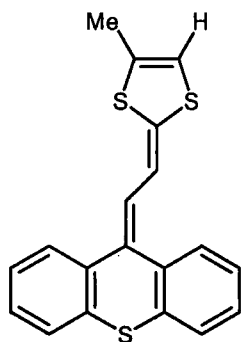
mixture was poured in ice water and neutralised to pH 7 by using 10% sodium hydroxide solution. The solution was extracted with chloroform, and the organic phase was dried over MgSO_4 and evaporated. The residue was chromatographed on silica (eluent, dichloromethane/ hexane 80/20) to afford compound **65** (1.44 g, 58%), yellow solid, mp: 108-110°C. ^1H NMR (CDCl_3): δ (ppm) 9.77 (d, 1H, $J=8$ Hz, *CHO*), 7.62 (m, 1H), 7.51 (d, 2H, $J=8$ Hz), 7.45 (m, 1H), 7.38 (t, 1H, $J=4$ Hz), 7.31 (m, 4H), 6.37 (d, 1H, $J=8$ Hz). ^{13}C NMR (CDCl_3): δ 193.29, 152.65, 134.11, 134.02, 132.14, 131.64, 129.83, 129.61, 129.35, 127.71, 127.66, 126.68, 126.51, 126.23, 126.21. MS (CI): m/z (%): 239 [M^+] (100). UV/Vis (CHCl_3): λ_{max} (lg ϵ) 386 (0.373) nm. $\text{C}_{15}\text{H}_{10}\text{OS}$ (238.05): calcd, C 75.60; H 4.23; found C 75.46, H 4.30.

9-[2-(4,5-Dimethyl-1,3-dithiol-2-ylidene)ethylidene]thioxanthene (66a)



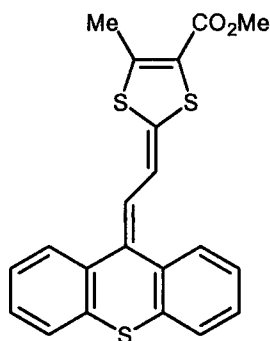
Following the general procedure for Wittig reaction, phosphonium salt **35a** (2.12 g, 8.72 mmol), BuLi (6 ml, 9.6 mmol), and compound **65** (2.07 g, 8.72 mmol) were stirred overnight. After evaporation and chromatography on silica (eluent, dichloromethane), and then on alumina (eluent, dichloromethane/ hexane 1:1) gave compound **66a** (2.0 g, 65%), red crystals, mp: 193-195° C. ¹H NMR (CDCl₃): δ (ppm) 7.51 (t, 2H, *J*=4 Hz), 7.40 (d, 1H, *J*=8 Hz), 7.34 (d, 1H, *J*=8 Hz), 7.26 (t, 2H, *J*=4 Hz), 7.20 (t, 2H, *J*=4 Hz), 6.43 (d, 2H, *J*=4 Hz), 1.94 (d, 6H, *J*=6 Hz, CH₃). ¹³C NMR (CDCl₃): δ 140.22, 138.63, 134.31, 133.73, 131.95, 130.06, 129.45, 127.26, 127.23, 127.08, 127.06, 126.99, 126.92, 126.64, 126.31, 126.08, 125.34, 122.20, 121.94, 109.11, 13.91, 13.90, 13.56, 13.55. MS (EI): *m/z* (%): 352 [M⁺] (100). UV/Vis (CHCl₃): λ_{max} (lgε) 423 (0.222) nm. C₂₀H₁₆S₃ (352.04): calcd, C 68.14; H 4.57; found C 67.86, H 4.57.

9-[2-(4-Methyl-1,3-dithiol-2-ylidene)ethylidene]thioxanthene (**66b**)



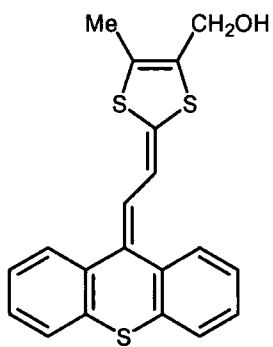
Following the general procedure for Wittig reaction, phosphonium salt (0.8 g, 3.48 mmol), BuLi (2.4 ml, 3.83 mmol), and compound **65** (0.83 g, 3.48 mmol) were stirred overnight. After evaporation and chromatography on silica (eluent, dichloromethane), and then on alumina (eluent, dichloromethane/ hexane 1:1) gave compound **66b** (0.657 g, 56%), yellow powder, mp: 163-165° C. ¹H NMR (CDCl₃): δ (ppm) 7.51 (t, 2H, *J*=4 Hz), 7.40 (d, 1H, *J*=4 Hz), 7.33 (d, 1H, *J*=4 Hz), 7.25 (m, 2H), 7.18 (m, 2H), 6.42 (d, 2H, *J*=4 Hz), 5.73 (s, 1H), 1.94 (d, 3H, *J*=6 Hz, CH₃). ¹³C NMR (CDCl₃): δ 140.22, 138.64, 134.31, 130.07, 129.45, 127.33, 127.06, 126.99, 126.92, 126.64, 126.31, 126.08, 125.34, 121.94, 109.12, 13.90, 13.55. MS (EI): *m/z* (%): 338 [M⁺] (100). UV/Vis (CHCl₃): λ_{max} (lgε) 391 (0.528) nm. C₁₉H₁₄S₃ (338.03): calcd, C 67.41; H 4.17; found C 67.26, H 4.45.

5-Methyl-2-(2-thioxanthen-9-ylidene-ethylidene)-1,3-dithiole-4-carboxylic acid methyl ester(**67**)



To a stirred solution of compound **66b** (1.85 g, 5.48 mmol) in dry THF under N₂ at -78°C, was added n-Butyllithium (ca. 1.6 in hexane) (3.77 ml, 6.03 mmol). The reaction mixture was stirred for 2 h. Methyl chloroformate (0.43 ml, 5.48 mmol) was added and the mixture was stirred and left to warm to room temperature overnight. The solvents are removed *in vacuo* and the residue was purified by chromatography on silica (eluent, dichloromethane/ hexane (75:25)) and a second one with dichloromethane/ hexane (50:50) as eluent to afford compound **67** (1.74 g, 80%), yellow crystals, mp: 97-99°C. ¹H NMR (CDCl₃): δ (ppm) 7.49 (d, 2H, *J*=6 Hz), 7.44 (d, 2H, *J*=6 Hz), 7.37 (d, 2H, *J*=6 Hz), 7.25 (m, 2H), 6.52 (dd, 2H, *J*=4 Hz, *J*=8 Hz, *CH*), 3.83 (s, 3H, CO₂CH₃), 2.40 (s, 3H, CH₃). ¹³C NMR (CDCl₃): δ 161.30, 152.29, 147.25, 138.11, 136.21, 133.86, 129.48, 129.24, 127.36, 127.30, 127.04, 126.98, 126.34, 126.10, 126.06, 126, 125.50, 125.36, 110.76, 52.73, 15.98. MS (EI): *m/z* (%): 396 [M⁺] (100). UV/Vis (CHCl₃): λ_{max} (lgε) 406 (0.549) nm. C₂₁H₁₆O₂S₃ (396.03): calcd, C 63.61; H 4.07; found C 63.38, H 4.03.

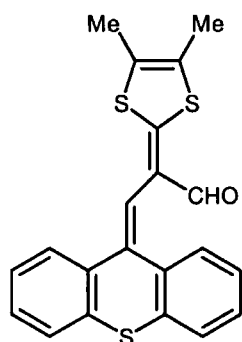
[5-Methyl-2-(2-thioxanthene-9-ylidene-ethylidene)-1,3-dithiol-4-yl]-methanol (**68**)



To a stirred solution of compound **67** (1.80 g, 4.53 mmol) in dry THF under N₂ at -78°C, was added lithium aluminium hydride (0.688 g, 18.14 mmol) and the resultant mixture was stirred for 2 h at 20°C. After adding wet dropwise of sodium sulphate (in excess), the reaction was stirred for 30 min.. The reaction mixture was filtered through Celite while washing with methanol. The evaporation of the filtrate gave compound **68** (1.17 g, 70%), yellow crystals, mp: 88-90°C. ¹H NMR (CDCl₃): δ (ppm) 7.55 (m, 2H), 7.48 (m, 2H), 7.40 (m, 2H), 7.30 (m, 2H), 6.52 (dd, 2H, *J*=4 Hz, *J*=8 Hz, *CH*), 4.20 (t, 2H, *J*=4 Hz, CH₂O), 1.97 (d, 3H, *J*=8 Hz, CH₃). ¹³C NMR (DMSO): δ 141.81, 141.75, 138.23, 133.74, 133.02, 131.32, 131.30, 130.74, 130.14, 129.74, 129.53, 129.37, 128.27, 128.07, 127.61, 127.45, 127.35, 127.08, 126.50, 125.76, 125.72, 124.17, 123.46, 108.77, 108.70, 57.10, 56.93, 14.03, 13.71. MS (EI): *m/z* (%): 368 [M⁺] (100). UV/Vis (CHCl₃): λ_{max}

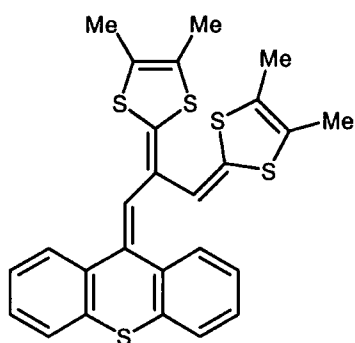
(lgε) 417 (0.309) nm. C₂₀H₁₆OS₃ (368.04): calcd, C 65.18; H 4.38; found C 65.11, H 4.42.

2-(4,5-Dimethyl-1,3-dithiol-2-ylidene)-3-thioxanthen-9-ylidene-propionaldehyde (69)



Phosphorus oxychloride (1.74 ml, 18.75 mmol) was added slowly to DMF (10 ml) cooled in an ice bath. To this mixture was slowly added a solution of compound **66a** (1.1 g, 3.12 mmol) in DMF (15 ml). The mixture was warmed to room temperature and was maintained at 60 °C overnight. The reaction mixture was poured in ice water and neutralised to pH 7 by using 10% sodium hydroxide solution. The solution was extracted with chloroform, and the organic phase was dried over MgSO₄ and evaporated. The residue was chromatographed on silica (eluent, dichloromethane/ hexane (1:1)). After evaporation, acetone was added and the resulting crude solid was filtered and washed with acetone to give compound **69** (1.18 g, 100%), yellow crystals, mp: 242-244 °C. ¹H NMR (CDCl₃): δ (ppm) 8.87 (s, 1H, CHO), 7.71 (d, 1H, *J*=4 Hz), 7.42 (d, 2H, *J*=4 Hz), 7.34 (q, 2H), 7.26 (m, 1H), 7.17 (t, 1H, *J*=4 Hz), 7.11 (t, 1H, *J*=4 Hz), 6.52 (s, 1H, CH), 2.21 (d, 6H, *J*=8 Hz, CH₃). ¹³C NMR (CDCl₃): δ 183.77, 137.25, 136.07, 134.28, 133.72, 132.69, 130.06, 128.77, 127.94, 127.42, 127.30, 127.23, 126.95, 126.44, 125.47, 124.34, 123.37, 116.85, 13.73, 13.41. IR (KBr) 2900, 1684, 1653, 1627, 1458, 1419, 1380, 1259, 858, 762, 739, 621, 543 cm⁻¹. MS (EI): *m/z* (%): 380 [M⁺] (89.43), 155 [M⁺-225] (100). UV/Vis (CHCl₃): λ_{max} (lgε) 429 (0.627) nm. C₂₁H₁₆OS₃ (380.04): calcd, C 66.28; H 4.24; found C 66.25, H 4.14.

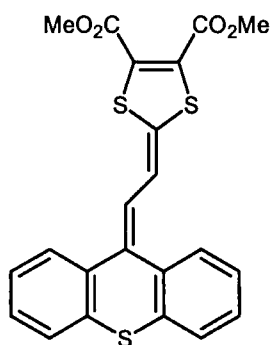
9-[2,3-Bis-(4,5-dimethyl-1,3-dithiol-2-ylidene)-propylidene]thioxanthene(70)



Following the general procedure for Wittig reaction, phosphonium salt **35a** (0.319 g, 1.31 mmol), BuLi (0.9 ml, 1.44 mmol), and compound **69** (0.5 g, 1.31 mmol) were stirred overnight. After evaporation and chromatography on silica (eluent, dichloromethane), recrystallisation from hexane gave compound **70** (0.15 g, 23%), red powder, mp: 201-203°C. ¹H NMR (CDCl₃): δ (ppm) 8.39 (dd, 2H, *J*=4 Hz, *J*=6 Hz), 8.19 (dd, 2H, *J*=4 Hz, *J*=6 Hz), 7.86 (t, 2H, *J*=4 Hz), 7.74 (t, 2H, *J*=4 Hz), 6.24 (s, 1H), 5.63 (s, 1H), 1.86 (s, 6H, CH₃), 1.80 (s, 6H, CH₃). ¹³C NMR (CDCl₃): δ

129.08, 128.91, 128.77, 127.48, 127.09, 126.62, 126.30, 125.87, 125.59, 113.84, 30.29, 29.94, 16.21, 14.51. MS (CI): *m/z* (%): 495 [M⁺] (5.77), 164 [M⁺-dimethyldithiol] (100). UV/Vis (CHCl₃): λ_{max} (lgε) 389 (0.205) nm, λ (lgε) 409 (0.200) nm. C₂₆H₂₂S₅ (494.03): calcd, C 63.11; H 4.48; found C 63.07, H 4.60.

2-(2-Thioxanthen-9-ylidene-ethylidene)-1,3-dithiole-4,5-dicarboxylic acid dimethyl ester (**71**)

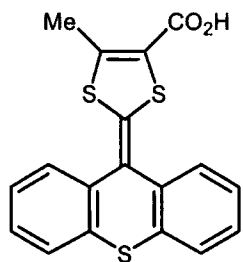


Following the general procedure for Wittig reaction, phosphonium salt **35d** (1.0, 2.73 mmol), BuLi (1.87 ml, 3.0 mmol), and compound **65** (0.65 g, 2.73 mmol) were stirred overnight. After evaporation, the chromatography on silica (eluent, dichloromethane) gave compound **71** (0.43 g, 39%), red crystals, mp: 196-198°C. ¹H NMR (CDCl₃): δ (ppm) 7.52 (d, 1H, *J*=4 Hz), 7.44 (m, 2H), 7.37 (d, 1H, *J*=4 Hz), 7.25 (m, 4H), 6.36 (dd, 2H, *J*=4 Hz, *J*=6 Hz), 3.85 (d, 6H, *J*=8 Hz, CO₂CH₃). ¹³C NMR (CDCl₃): δ

160.28, 159.95, 137.66, 134.55, 133.90, 133.40, 133.26, 132.28, 132.03, 130.14, 129.47, 127.62, 127.36, 127.23, 127, 126.43, 126.14, 125.46, 125.31, 112.83, 53.70, 53.68, 53.62. MS (CI): *m/z* (%): 440 [M⁺] (100). UV/Vis (CHCl₃): λ_{max} (lgε) 398 (0.317) nm. C₂₂H₁₆O₄S₅ (440.02): calcd, C 59.98; H 3.66; found C 59.95, H 3.49.

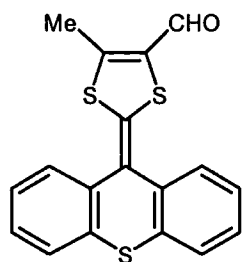
Experimental Procedure for Chapter Four

5-Methyl-2-thioxanthen-9-ylidene-1,3-dithiole-4-carboxylic acid (**79**)



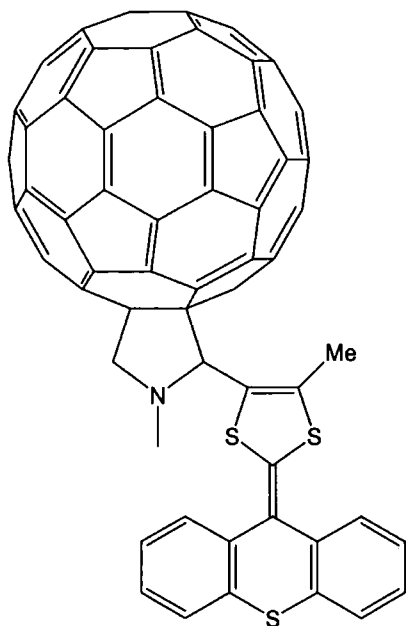
To a stirred solution of compound **36** (0.3 g, 0.8 mmol) in a mixture of methanol:THF, 90:10, potassium hydroxide (0.046 g, 0.8 mmol) was added, and the mixture was refluxed overnight. The solution was cooled to 0°C, followed by successive addition of water and hydrochloric acid to reach an acidic pH. The precipitate was filtered and wash with water to give compound **79** (0.175 g, 60%), yellow powder, mp: 195-197°C. ¹H NMR (DMSO): δ (ppm) 7.53 (m, 4H), 7.35 (m, 4H), 2.35 (s, 3H, CH₃). ¹³C NMR (DMSO): δ 160.94, 135.42, 132.16, 131.11, 126.88, 126.52, 121.89, 14.95. MS (EI): m/z (%): 356 [M⁺] (100). UV/Vis (CHCl₃): λ_{max} (lgε) 368 (0.213) nm. C₁₈H₁₂O₂S₃ (356.00): calcd, C 60.65; H 3.39; found C 60.70, H 3.69.

5-Methyl-2-thioxanthen-9-ylidene-1,3-dithiole-4-carbaldehyde (**81**)



The acid chloride **80** (0.52 g, 1.38 mmol) was dissolved in dry THF. The solution was cooled to -78°C and lithium tri-tert-butoxyaluminumhydride (0.13 ml, 1.52 mmol) was added dropwise. The reaction was stirred at -78°C for few minutes then allowed to reach room temperature. Evaporation of the solvent and purification by column chromatography (eluent, dichloromethane) gave **81** (0.09 g, 19%), yellow solid, mp: 157-159°C. ¹H NMR (CDCl₃): δ (ppm) 9.67 (s, 1H, CHO), 7.59 (m, 2H), 7.43 (m, 2H), 7.31 (m, 2H), 7.25 (m, 2H), 2.39 (s, 3H, CH₃). ¹³C NMR (CDCl₃): δ 178.77, 151.01, 136.21, 136.14, 132.83, 132.33, 132.13, 131.33, 127.72, 127.67, 127.32, 127.20, 126.95, 126.64, 126.57, 126.29, 124.63, 13.85. MS (EI): m/z (%): 340 [M⁺] (100). UV/Vis (CHCl₃): λ_{max} (lgε) 361 (0.143) nm, λ (lgε) 428 (0.067) nm. C₁₈H₁₂OS₃ (340.01): calcd, C 63.50; H 3.55; found C 63.54, H 3.52.

Compound (82)

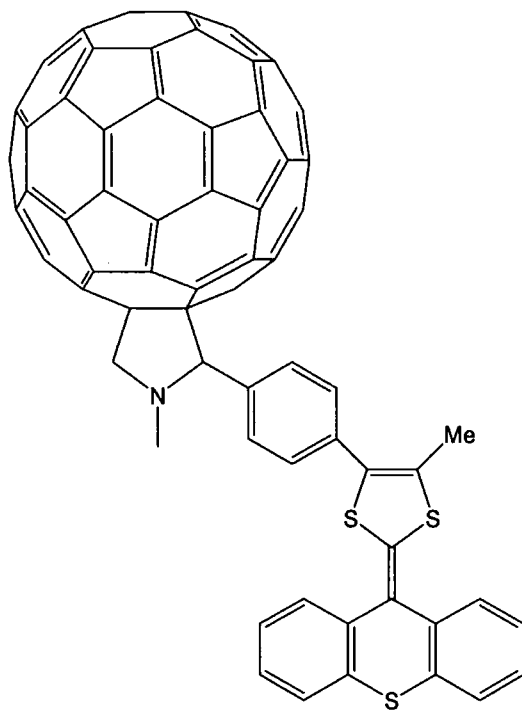


Compound **81** (0.105 g, 0.3 mmol), C_{60} (0.222 g, 0.3 mmol), and sarcosine (0.055 g, 0.6 mmol) were added to dry toluene, and the mixture was refluxed for 48 h. The solvent was removed *in vacuo* and the residue was purified by column chromatography (eluent, carbon disulfide) to give compound **82** (0.055 g, 16%), black powder, FW: 1087, mp: $>250^{\circ}\text{C}$. ^1H NMR (CDCl_3): δ (ppm) 8.79 (d, 2H, $J=8$ Hz), 7.21 (d, 2H, $J=4$ Hz), 7.13 (m, 4H), 4.88 (s, 1H), 4.45 (d, 1H, $J=8$ Hz), 3.78 (d, 1H, $J=4$ Hz), 2.55 (s, 3H, $N\text{CH}_3$), 2.01 (s, 3H, CH_3). UV/Vis (CHCl_3): λ_{max} (lg ϵ) 314 (1.24), 381 (0.71), 436 (0.13), 713 (0.006), 875 (0.02), 911 (0.01) nm. IR (KBr) 2914, 2784, 1734, 1640, 1596, 1506, 1464, 1319, 762, 735, 526 cm^{-1} .

Compound (83) (2:1 adduct)

83: $\text{C}_{100}\text{H}_{34}\text{N}_2\text{S}_6$, FW: 1454, brown powder, mp: $>250^{\circ}\text{C}$. ^1H NMR (CDCl_3): δ (ppm) 8.79 (d, 2H, $J=8$ Hz), 7.21 (d, 2H, $J=4$ Hz), 7.13 (m, 4H), 4.88 (s, 1H), 4.45 (d, 1H, $J=8$ Hz), 3.78 (d, 1H, $J=4$ Hz), 2.55 (s, 3H, $N\text{CH}_3$), 2.01 (s, 3H, CH_3). UV/Vis (CHCl_3): λ_{max} (lg ϵ) 369 (0.96), 713 (0.004), 875 (0.026), 911 (0.009) nm. IR (KBr) 2952, 2781, 2372, 2340, 1740, 1662, 1646, 1562, 1457, 1440, 766, 737, 526 cm^{-1} .

Compound (84)



Compound **56** (0.244 g, 0.58 mmol), C_{60} (0.42 g, 0.58 mmol), and sarcosine (0.104 g, 1.16 mmol) were added to dry toluene, and the mixture was refluxed for 48 h. The solvent was removed *in vacuo* and the residue was purified by column chromatography (eluent, carbon disulfide) to give compound **84** (0.092g, 13%), black powder, FW: 1163, mp: 181-183°C. 1H NMR ($CDCl_3$): δ (ppm) 8.63 (d, 2H, $J=8$ Hz), 7.62 (m, 6H), 7.50 (t, 3H, $J=4$ Hz, $J=6$ Hz), 7.42 (d, 1H, $J=4$ Hz), 5.00 (t, 2H, $J=4$ Hz), 4.29 (d, 1H, $J=8$ Hz), 2.83 (s, 3H, NCH_3), 2.18 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$): δ 180.24, 147.59, 146.75, 146.62,

146.56, 146.48, 146.38, 146.21, 146.11, 145.95, 145.76, 145.60, 145.54, 145.49, 144.97, 144.78, 144.66, 144.58, 143.42, 143.27, 142.97, 142.86, 142.47, 142.42, 142.29, 142.18, 142.13, 142.06, 141.95, 141.79, 140.45, 140.15, 139.60, 137.53, 132.53, 130.13, 129.48, 126.56, 126.24, 83.27, 70.31, 68.93, 40.31, 30.21, 15.60. UV/Vis ($CHCl_3$): λ_{max} (lg ϵ) 374 (0.62), 433 (0.13), 704 (0.004), 874 (0.02), 909 (0.008) nm. IR (KBr) 2922, 2788, 2372, 2348, 1653, 1640, 1596, 1507, 1458, 1324, 736, 669, 526 cm^{-1} .

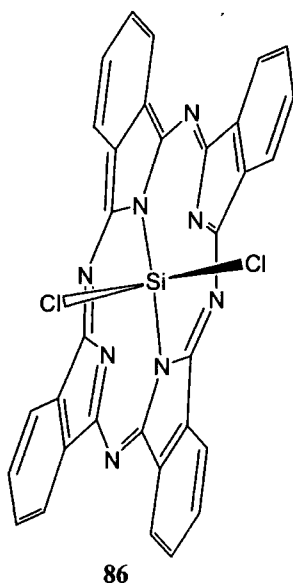
Compound (85) (2:1 adduct)

85: $C_{112}H_{42}N_2S_6$, FW: 1606, brown powder, mp: >250°C. 1H NMR ($CDCl_3$): δ (ppm) 8.63 (d, 2H, $J=8$ Hz), 7.62 (m, 6H), 7.50 (t, 3H, $J=4$ Hz), 7.42 (d, 1H, $J=8$ Hz), 5.00 (t, 2H, $J=8$ Hz), 4.29 (d, 1H, $J=8$ Hz), 2.83 (s, 3H, NCH_3), 2.18 (s, 3H, CH_3). UV/Vis ($CHCl_3$): λ_{max} (lg ϵ) 379 (0.79), 714 (0.014), 874 (0.039), 911 (0.023) nm. IR (KBr) 2952, 2778, 2368, 2340, 1645, 1596, 1440, 1324, 1168, 1128, 1036, 766, 740, 670, 525 cm^{-1} .

APPENDIX ONE

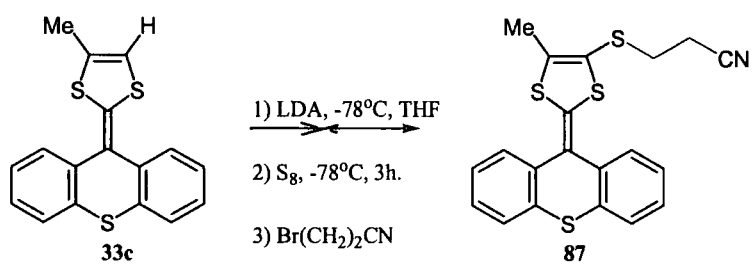
ATTEMPTED LINKAGE TO PHTHALOCYANINES:

Phthalocyanines (pcs) and their macrocyclic analogues continue to attract considerable attention, due in part to their characteristic optical properties, and applications including medicinal therapeutic agents, photosensitisers, photoconductors, catalysts and non-linear optical devices have been demonstrated ^[1]. Despite the fact that many *peripherally* substituted pcs have been synthesised, with equatorial groups including ferrocenes, crown ethers, dendrimers, and sugars and biologically active nucleobases, there are relatively few *axially* substituted silicon pcs ^[2]. Derivatives substituted in this way are not able to aggregate in solution and have higher quantum yields and fluorescence lifetimes than the more common zinc or aluminium pcs. Furthermore, pcs have long been known to undergo electron transfer reactions, both to and from their excited states, and previous work in our group has shown that strong electron donors such as TTF are able to quench the pc fluorescence by intermolecular electron transfer, and covalent TTF-pc hybrids, prepared from silicon phthalocyanine dichloride **86**, have proved to be interesting materials for detailed photophysical studies ^[3].



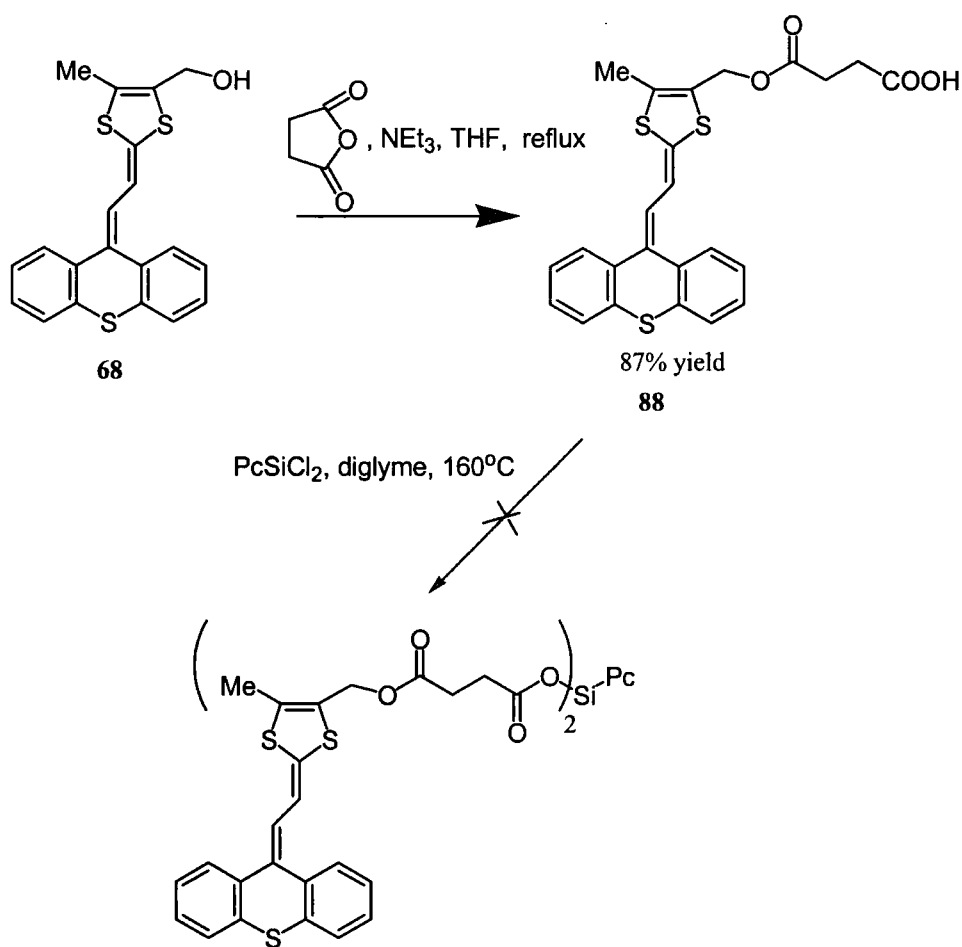
Silicon Phthalocyanine Dichloride.

We, therefore, considered that it would be of interest to synthesise hybrids of pc with derivatives of **33c**. We first attempted to prepare the (2-cyanoethyl)sulfanyl derivative **87** of **33c** via sulphur insertion ^[4, 5] into the lithiated species, followed by reaction with 3-bromopropionitrile (Scheme 1). We planned to use the thiolate anion derived from **87** as a nucleophilic building block, but unfortunately, despite several attempts, compound **87** could never be isolated, and only starting material **33c** was recovered. Other workers in our laboratory have found previously that sulfur insertion into lithiated TTF derivatives can be capricious, and success appears to depend critically on the quality of the sulphur used, and other conditions which are not well understood ^[6].



Scheme 1.

In a different approach, from previous experiments (Chapter 2), we knew that compound **33c** generates the corresponding anion, so we attempted the direct coupling between this species and silicon pc dichloride in di(methoxyethyl)ether ^[3], but no reaction occurred. We tried also with the hydroxymethyl **37** and carboxylic acid **79** derivatives under the same conditions but without any success. We then concluded that steric hindrance of the bulky silicon pc might be preventing reaction from occurring and that this could be overcome if a spacer group was incorporated. Consequently, we synthesised the terminal carboxylic acid derivative **88** (87% yield) by reaction of succinic anhydride on the hydroxymethyl derivative **68** in presence of triethylamine in dry THF (Scheme 2).



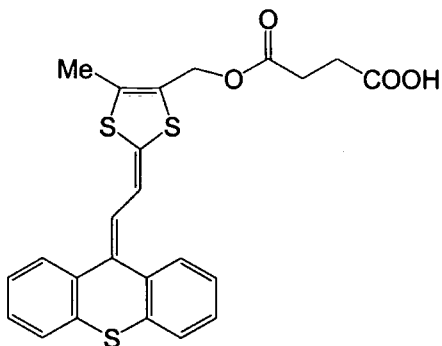
Scheme 2.

A mixture of silicon pc dichloride **86** and the acid derivative **88** in di(methoxyethyl)ether was heated at 160°C overnight, as reported for TTF analogues^[3]. After quenching of the solution with water, we did not isolate any characterisable product as we got a black mess.

Curiously, we have not been able to synthesise any pc hybrids with derivatives of **33c**. It is presumably due either to a lack of reactivity of our reagents derived from **33c** with **86**, or due to instability of the products formed, which would explain why we did not recover any starting material from the black mess produced in each of the attempted reactions.

Experimental Procedure

Succinic acid mono-[5-methyl-2-(2-thioxanthen-9-ylidene-ethylidene)-1,3-dithiol-4-ylmethyl]ester (**88**)



To a stirred solution of **68** (0.202 g, 0.54 mmol) and succinic anhydride (0.054 g, 0.54 mmol) in dry THF, was added triethylamine (0.08 ml, 0.54 mmol), the mixture was refluxed overnight. The solvent was removed under vacuum and the residue was purified by column chromatography with DCM as eluent to give compound **88** (0.215 g, 87%),

yellow powder, mp: 68-70°C. ^1H NMR (CDCl_3): δ (ppm) 7.44 (q, 1H), 7.30 (dd, 2H, $J=7.99$ Hz, $J=7.99$ Hz), 7.16 (m, 4H), 6.46 (d, 1H, $J=15.99$ Hz), 6.24 (d, 1H, $J=15.99$ Hz), 4.74 (d, 2H, $J=15.99$ Hz), 2.60 (m, 4H), 1.98 (s, 3H). ^{13}C NMR (CDCl_3): δ 177.28, 171.96, 138.57, 134.08, 133.80, 131.94, 131.04, 130.73, 130.13, 129.47, 127.30, 127.27, 126.95, 126.82, 126.58, 126.53, 126.34, 126.08, 125.45, 125.36, 121.86, 121.53, 110.34, 110.20, 60.68, 58.72, 58.53, 28.89, 21.31, 14.44, 14.19, 13.84. MS (CI): m/z (%): 221 [M^+-247] (100), 468 [M^+] (19.46). UV/Vis (CHCl_3): λ_{max} (lg ϵ) 421 (0.987) nm.

$\text{C}_{24}\text{H}_{20}\text{O}_4\text{S}_3$ (468.05): calcd, C 61.51; H 4.30; found C 61.47, H 4.33.

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APPENDIX TWO

X-RAY CRYSTALLOGRAPHIC DATA

9-(4,5-Dimethyl-1,3dithiol-2-ylidene)thioxanthene (33a)

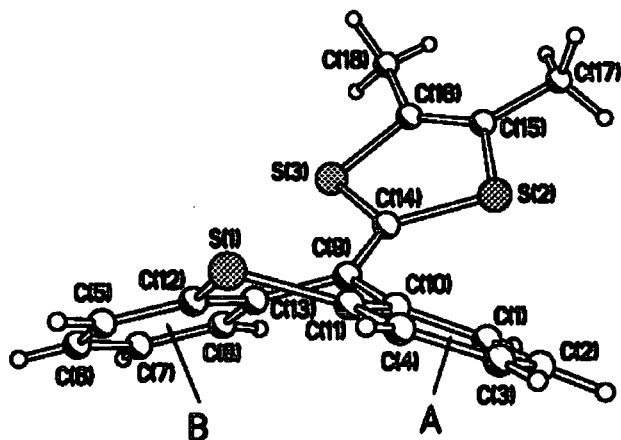


Table 1. Crystal data and structure refinement.

Empirical formula	C18 H14 S3	
Formula weight	326.47	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$ (No. 14, non-standard setting)	
Unit cell dimensions	$a = 9.978(2)$ Å	$\alpha = 90^\circ$
	$b = 7.797(1)$ Å	$\beta = 91.87(1)^\circ$
	$c = 19.429(3)$ Å	$\gamma = 90^\circ$
Volume	$1510.7(4)$ Å ³	
Z	4	
Density (calculated)	1.435 g/cm ³	
Absorption coefficient	0.480 mm ⁻¹	
F(000)	680	
Crystal size	$0.40 \times 0.30 \times 0.08$ mm ³	
θ range for data collection	2.10 to 27.54° .	
Index ranges	$-12 \leq h \leq 12$, $-10 \leq k \leq 10$, $-22 \leq l \leq 25$	
Reflections collected	15639	

Independent reflections	3475 [R(int) = 0.0572]
Reflections with $I > 2\sigma(I)$	2885
Completeness to $\theta = 27.54^\circ$	100.0 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3475 / 0 / 246
Largest final shift/e.s.d. ratio	0.000
Goodness-of-fit on F^2	1.080
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0339, wR2 = 0.0788
R indices (all data)	R1 = 0.0451, wR2 = 0.0850
Largest diff. peak and hole	0.434 and -0.298 e.Å ⁻³

Table 2. Bond lengths [Å] and angles [°].

S(1)-C(11)	1.7579(19)	C(6)-H(6)	0.93(2)
S(1)-C(12)	1.7587(18)	C(7)-C(8)	1.384(3)
S(2)-C(15)	1.7556(18)	C(7)-H(7)	0.94(2)
S(2)-C(14)	1.7584(19)	C(8)-C(13)	1.404(3)
S(3)-C(16)	1.7537(19)	C(8)-H(8)	0.95(2)
S(3)-C(14)	1.7621(18)	C(9)-C(14)	1.360(2)
C(1)-C(2)	1.388(3)	C(9)-C(13)	1.477(2)
C(1)-C(10)	1.397(3)	C(9)-C(10)	1.484(2)
C(1)-H(1)	0.96(2)	C(10)-C(11)	1.403(2)
C(2)-C(3)	1.385(3)	C(12)-C(13)	1.402(2)
C(2)-H(2)	0.97(2)	C(15)-C(16)	1.335(3)
C(3)-C(4)	1.378(3)	C(15)-C(17)	1.493(3)
C(3)-H(3)	0.93(2)	C(16)-C(18)	1.499(3)
C(4)-C(11)	1.398(2)	C(17)-H(17C)	0.99(3)
C(4)-H(4)	0.95(2)	C(17)-H(17B)	0.95(3)
C(5)-C(6)	1.382(3)	C(17)-H(17A)	0.98(3)
C(5)-C(12)	1.397(3)	C(18)-H(18C)	0.92(3)
C(5)-H(5)	0.94(2)	C(18)-H(18B)	0.97(3)
C(6)-C(7)	1.389(3)	C(18)-H(18A)	0.99(3)
C(11)-S(1)-C(12)	101.00(9)	C(15)-S(2)-C(14)	97.25(9)

C(16)-S(3)-C(14)	97.20(9)	C(4)-C(11)-C(10)	120.88(17)
C(2)-C(1)-C(10)	121.02(17)	C(4)-C(11)-S(1)	116.37(14)
C(2)-C(1)-H(1)	119.7(13)	C(10)-C(11)-S(1)	122.75(14)
C(10)-C(1)-H(1)	119.2(13)	C(5)-C(12)-C(13)	121.03(16)
C(3)-C(2)-C(1)	120.35(18)	C(5)-C(12)-S(1)	117.26(14)
C(3)-C(2)-H(2)	120.1(12)	C(13)-C(12)-S(1)	121.70(14)
C(1)-C(2)-H(2)	119.5(12)	C(12)-C(13)-C(8)	117.18(17)
C(4)-C(3)-C(2)	119.89(17)	C(12)-C(13)-C(9)	120.58(16)
C(4)-C(3)-H(3)	119.2(14)	C(8)-C(13)-C(9)	122.21(16)
C(2)-C(3)-H(3)	120.8(14)	C(9)-C(14)-S(2)	125.24(14)
C(3)-C(4)-C(11)	119.96(17)	C(9)-C(14)-S(3)	123.00(14)
C(3)-C(4)-H(4)	119.4(13)	S(2)-C(14)-S(3)	111.60(10)
C(11)-C(4)-H(4)	120.6(13)	C(16)-C(15)-C(17)	127.45(17)
C(6)-C(5)-C(12)	120.29(18)	C(16)-C(15)-S(2)	116.70(15)
C(6)-C(5)-H(5)	121.0(14)	C(17)-C(15)-S(2)	115.84(14)
C(12)-C(5)-H(5)	118.7(14)	C(15)-C(16)-C(18)	127.75(18)
C(5)-C(6)-C(7)	119.71(18)	C(15)-C(16)-S(3)	116.69(14)
C(5)-C(6)-H(6)	121.3(13)	C(18)-C(16)-S(3)	115.56(15)
C(7)-C(6)-H(6)	119.0(13)	C(15)-C(17)-H(17C)	111.8(14)
C(8)-C(7)-C(6)	119.94(18)	C(15)-C(17)-H(17B)	108.4(15)
C(8)-C(7)-H(7)	119.0(14)	H(17C)-C(17)-H(17B)	109(2)
C(6)-C(7)-H(7)	121.0(14)	C(15)-C(17)-H(17A)	110.2(15)
C(7)-C(8)-C(13)	121.77(17)	H(17C)-C(17)-H(17A)	112(2)
C(7)-C(8)-H(8)	118.9(13)	H(17B)-C(17)-H(17A)	106(2)
C(13)-C(8)-H(8)	119.3(13)	C(16)-C(18)-H(18C)	110.9(17)
C(14)-C(9)-C(13)	121.42(16)	C(16)-C(18)-H(18B)	112.5(15)
C(14)-C(9)-C(10)	121.75(16)	H(18C)-C(18)-H(18B)	109(2)
C(13)-C(9)-C(10)	116.66(15)	C(16)-C(18)-H(18A)	113.3(15)
C(1)-C(10)-C(11)	117.72(16)	H(18C)-C(18)-H(18A)	106(2)
C(1)-C(10)-C(9)	123.10(16)	H(18B)-C(18)-H(18A)	105(2)
C(11)-C(10)-C(9)	119.18(16)		

9-(4,5-Dimethyl-1,3-dithiol-2-ylidene)thioxanthene 10,10-dioxide (52) .1/2 ethyl acetate

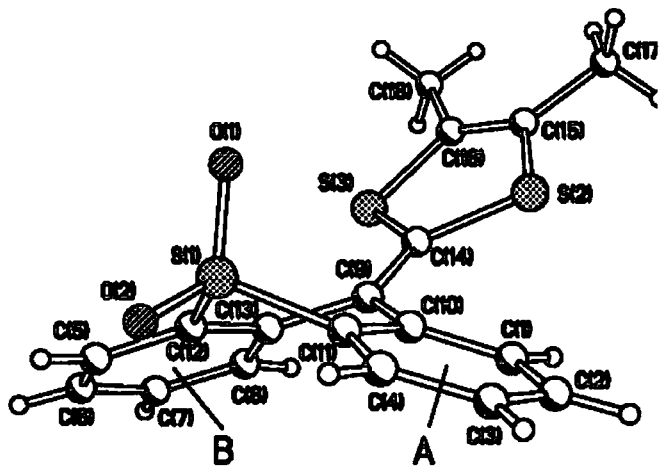


Table 1. Crystal data and structure refinement.

Empirical formula	C20 H18 O3 S3	
Formula weight	402.52	
Temperature	120(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	$P\bar{1}$ (No. 2)	
Unit cell dimensions	$a = 7.713(1)$ Å	$\alpha = 81.42(1)^\circ$
	$b = 10.907(1)$ Å	$\beta = 77.72(1)^\circ$
	$c = 12.042(1)$ Å	$\gamma = 71.13(1)^\circ$
Volume	933.1(2) Å ³	
Z	2	
Density (calculated)	1.433 g/cm ³	
Absorption coefficient	0.415 mm ⁻¹	
F(000)	420	
Crystal size	0.5 × 0.35 × 0.2 mm ³	
θ range for data collection	1.73 to 29.06°.	
Index ranges	-10 ≤ h ≤ 10, -14 ≤ k ≤ 14, -16 ≤ l ≤ 16	
Reflections collected	11372	
Independent reflections	4878 [R(int) = 0.0370]	

Reflections with $I > 2\sigma(I)$	4417
Completeness to $\theta = 29.06^\circ$	97.5 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4878 / 0 / 265
Largest final shift/e.s.d. ratio	0.001
Goodness-of-fit on F^2	1.030
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0319$, $wR2 = 0.0842$
R indices (all data)	$R1 = 0.0354$, $wR2 = 0.0877$
Largest diff. peak and hole	0.307 and -0.440 e. \AA^{-3}
Disorder: Ethyl acetate molecule [the atoms O(3), O(4), C(19), C(20), C(21), C(22)] is disordered between two positions, related via an inversion centre.	

Table 2. Bond lengths [\AA] and angles [$^\circ$].

S(1)-O(2)	1.4425(10)	C(7)-C(8)	1.389(2)
S(1)-O(1)	1.4444(10)	C(8)-C(13)	1.4019(17)
S(1)-C(12)	1.7533(14)	C(9)-C(14)	1.3686(15)
S(1)-C(11)	1.7556(12)	C(9)-C(10)	1.4774(15)
S(2)-C(14)	1.7504(13)	C(9)-C(13)	1.4815(16)
S(2)-C(15)	1.7609(14)	C(10)-C(11)	1.4081(15)
S(3)-C(14)	1.7532(12)	C(12)-C(13)	1.4064(17)
S(3)-C(16)	1.7551(15)	C(15)-C(16)	1.334(2)
C(1)-C(2)	1.3905(17)	C(15)-C(17)	1.508(2)
C(1)-C(10)	1.4003(16)	C(16)-C(18)	1.506(2)
C(2)-C(3)	1.3917(19)	O(3)-C(19)	1.347(3)
C(3)-C(4)	1.3856(19)	O(3)-C(21)	1.452(4)
C(4)-C(11)	1.3918(16)	O(4)-C(19)	1.196(4)
C(5)-C(6)	1.385(2)	C(19)-C(20)	1.498(4)
C(5)-C(12)	1.3932(18)	C(21)-C(22)	1.490(6)
C(6)-C(7)	1.384(3)		
O(2)-S(1)-O(1)	117.49(7)	O(1)-S(1)-C(11)	108.38(6)
O(2)-S(1)-C(12)	109.82(7)	C(12)-S(1)-C(11)	100.64(6)
O(1)-S(1)-C(12)	109.07(6)	C(14)-S(2)-C(15)	97.12(7)
O(2)-S(1)-C(11)	110.11(6)	C(14)-S(3)-C(16)	97.30(7)

C(2)-C(1)-C(10)	120.78(11)	C(13)-C(12)-S(1)	117.95(9)
C(1)-C(2)-C(3)	121.19(12)	C(8)-C(13)-C(12)	116.74(11)
C(4)-C(3)-C(2)	119.40(11)	C(8)-C(13)-C(9)	122.83(11)
C(3)-C(4)-C(11)	119.10(11)	C(12)-C(13)-C(9)	120.34(11)
C(6)-C(5)-C(12)	119.07(14)	C(9)-C(14)-S(2)	124.90(9)
C(7)-C(6)-C(5)	119.85(13)	C(9)-C(14)-S(3)	123.04(9)
C(6)-C(7)-C(8)	120.80(14)	S(2)-C(14)-S(3)	111.91(6)
C(7)-C(8)-C(13)	121.02(14)	C(16)-C(15)-C(17)	128.01(14)
C(14)-C(9)-C(10)	122.65(10)	C(16)-C(15)-S(2)	116.58(10)
C(14)-C(9)-C(13)	120.88(10)	C(17)-C(15)-S(2)	115.40(13)
C(10)-C(9)-C(13)	116.37(10)	C(15)-C(16)-C(18)	129.02(15)
C(1)-C(10)-C(11)	116.72(10)	C(15)-C(16)-S(3)	116.44(10)
C(1)-C(10)-C(9)	123.11(10)	C(18)-C(16)-S(3)	114.53(14)
C(11)-C(10)-C(9)	120.09(10)	C(19)-O(3)-C(21)	116.0(2)
C(4)-C(11)-C(10)	122.76(11)	O(4)-C(19)-O(3)	123.6(3)
C(4)-C(11)-S(1)	119.24(9)	O(4)-C(19)-C(20)	125.0(3)
C(10)-C(11)-S(1)	117.84(9)	O(3)-C(19)-C(20)	111.4(3)
C(5)-C(12)-C(13)	122.39(13)	O(3)-C(21)-C(22)	106.6(3)
C(5)-C(12)-S(1)	119.64(11)		

9-[2-(4,5-Dimethyl-1,3-dithiol-2-ylidene)-ethylidene]thioxanthene (66a)

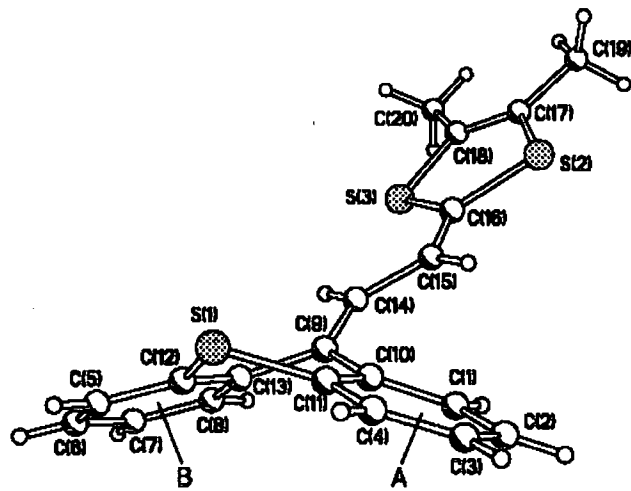


Table 1. Crystal data and structure refinement.

Empirical formula	C ₂₀ H ₁₆ S ₃	
Formula weight	352.51	
Temperature	120(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	<i>P</i> 2 ₁ / <i>n</i> (No. 14 non-standard setting)	
Unit cell dimensions	<i>a</i> = 9.590(1) Å	α = 90°
	<i>b</i> = 7.659(1) Å	β = 101.06(1)°
	<i>c</i> = 23.140(3) Å	γ = 90°
Volume	1668.1(4) Å ³	
<i>Z</i>	4	
Density (calculated)	1.404 g/cm ³	
Absorption coefficient	0.440 mm ⁻¹	
<i>F</i> (000)	736	
Crystal size	0.6 × 0.4 × 0.2 mm ³	
θ range for data collection	1.79 to 30.00°.	
Index ranges	-13 ≤ <i>h</i> ≤ 13, -10 ≤ <i>k</i> ≤ 10, -32 ≤ <i>l</i> ≤ 32	
Reflections collected	22899	
Independent reflections	4785 [R(int) = 0.0407]	

Reflections with $I > 2\sigma(I)$	3833
Completeness to $\theta = 30.00^\circ$	98.3 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4785 / 0 / 249
Largest final shift/e.s.d. ratio	0.001
Goodness-of-fit on F^2	1.057
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0412$, $wR2 = 0.1092$
R indices (all data)	$R1 = 0.0537$, $wR2 = 0.1147$
Largest diff. peak and hole	0.444 and -0.289 e. \AA^{-3}
Disorder: Atoms S(2), S(3), C(14), C(15), C(16), C(17), C(18), C(19), C(20) with their hydrogens are disordered between two positions, with occupancies 88.4(1)% (unprimed) and 11.6(1)% (primed).	

Table 2. Bond lengths [\AA] bond and torsion angles [$^\circ$].

S(1)-C(12)	1.7615(19)	C(7)-C(8)	1.385(2)
S(1)-C(11)	1.7618(19)	C(8)-C(13)	1.401(2)
S(2)-C(17)	1.7523(18)	C(9)-C(14)	1.359(2)
S(2)-C(16)	1.7565(19)	C(9)-C(14')	1.47(2)
S(3)-C(16)	1.7445(18)	C(9)-C(13)	1.474(2)
S(3)-C(18)	1.7562(19)	C(9)-C(10)	1.480(2)
S(2')-C(16')	1.646(15)	C(10)-C(11)	1.407(2)
S(2')-C(17')	1.859(17)	C(12)-C(13)	1.408(2)
S(3')-C(16')	1.785(16)	C(14)-C(15)	1.439(3)
S(3')-C(18')	1.825(17)	C(15)-C(16)	1.359(2)
C(1)-C(2)	1.381(2)	C(17)-C(18)	1.338(3)
C(1)-C(10)	1.396(2)	C(17)-C(19)	1.504(3)
C(2)-C(3)	1.394(3)	C(18)-C(20)	1.512(3)
C(3)-C(4)	1.374(3)	C(14')-C(15')	1.39(2)
C(4)-C(11)	1.398(3)	C(15')-C(16')	1.43(2)
C(5)-C(6)	1.379(3)	C(17')-C(18')	1.23(2)
C(5)-C(12)	1.401(2)	C(17')-C(19')	1.48(2)
C(6)-C(7)	1.390(3)	C(18')-C(20')	1.49(3)
C(12)-S(1)-C(11)	100.35(8)	C(17)-S(2)-C(16)	96.87(10)

C(16)-S(3)-C(18)	97.00(12)	C(13)-C(12)-S(1)	121.00(13)
C(16')-S(2')-C(17')	94.5(9)	C(8)-C(13)-C(12)	118.36(15)
C(16')-S(3')-C(18')	93.5(8)	C(8)-C(13)-C(9)	122.02(13)
C(2)-C(1)-C(10)	122.21(16)	C(12)-C(13)-C(9)	119.60(15)
C(1)-C(2)-C(3)	119.34(18)	C(9)-C(14)-C(15)	127.0(2)
C(4)-C(3)-C(2)	119.99(17)	C(16)-C(15)-C(14)	123.00(18)
C(3)-C(4)-C(11)	120.65(16)	C(15)-C(16)-S(3)	125.17(14)
C(6)-C(5)-C(12)	119.97(16)	C(15)-C(16)-S(2)	122.20(14)
C(5)-C(6)-C(7)	120.66(17)	S(3)-C(16)-S(2)	112.62(10)
C(8)-C(7)-C(6)	119.67(18)	C(18)-C(17)-C(19)	127.01(16)
C(7)-C(8)-C(13)	121.13(15)	C(18)-C(17)-S(2)	116.66(17)
C(14)-C(9)-C(14')	18.9(7)	C(19)-C(17)-S(2)	116.28(16)
C(14)-C(9)-C(13)	118.82(17)	C(17)-C(18)-C(20)	127.13(17)
C(14')-C(9)-C(13)	137.6(8)	C(17)-C(18)-S(3)	116.68(19)
C(14)-C(9)-C(10)	124.89(17)	C(20)-C(18)-S(3)	116.2(2)
C(14')-C(9)-C(10)	106.2(7)	C(15')-C(14')-C(9)	113.5(14)
C(13)-C(9)-C(10)	116.24(13)	C(14')-C(15')-C(16')	113.6(15)
C(1)-C(10)-C(11)	117.49(15)	C(15')-C(16')-S(2')	128.5(12)
C(1)-C(10)-C(9)	122.53(13)	C(15')-C(16')-S(3')	114.6(11)
C(11)-C(10)-C(9)	119.92(15)	S(2')-C(16')-S(3')	116.9(9)
C(4)-C(11)-C(10)	120.24(17)	C(18')-C(17')-C(19')	129.5(17)
C(4)-C(11)-S(1)	119.13(13)	C(18')-C(17')-S(2')	117.9(16)
C(10)-C(11)-S(1)	120.61(13)	C(19')-C(17')-S(2')	112.5(15)
C(5)-C(12)-C(13)	120.17(17)	C(17')-C(18')-C(20')	127(2)
C(5)-C(12)-S(1)	118.72(13)	C(17')-C(18')-S(3')	116.8(15)
C(20')-C(18')-S(3')	115.8(16)		
C(10)-C(9)-C(14)-C(15)	-6.6(3)	C(13)-C(9)-C(14')-C(15')	3(2)
C(9)-C(14)-C(15)-C(16)	-176.93(17)	C(9)-C(14')-C(15')-C(16')	173.3(12)
C(14)-C(15)-C(16)-S(3)	-3.9(2)	C(14')-C(15')-C(16')-S(2')	-2(2)

